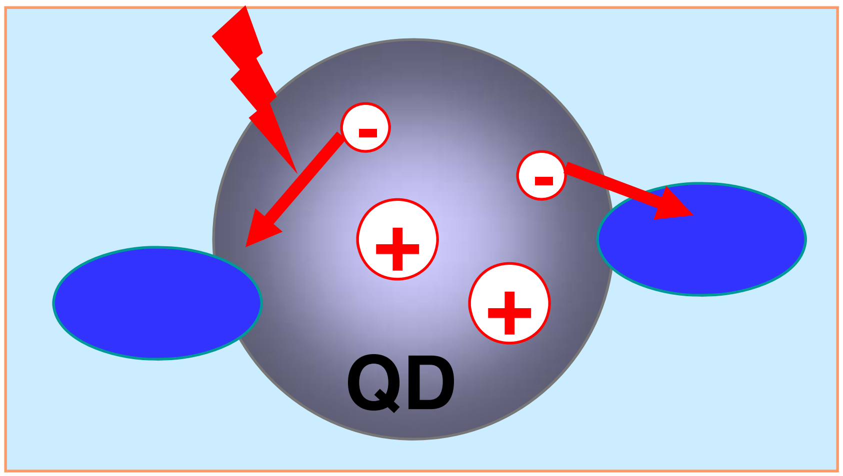
Ultrafast Electron Transfer from Quantum Dots: towards Multi-Exciton Dissociation



University of Massachusetts Amherst

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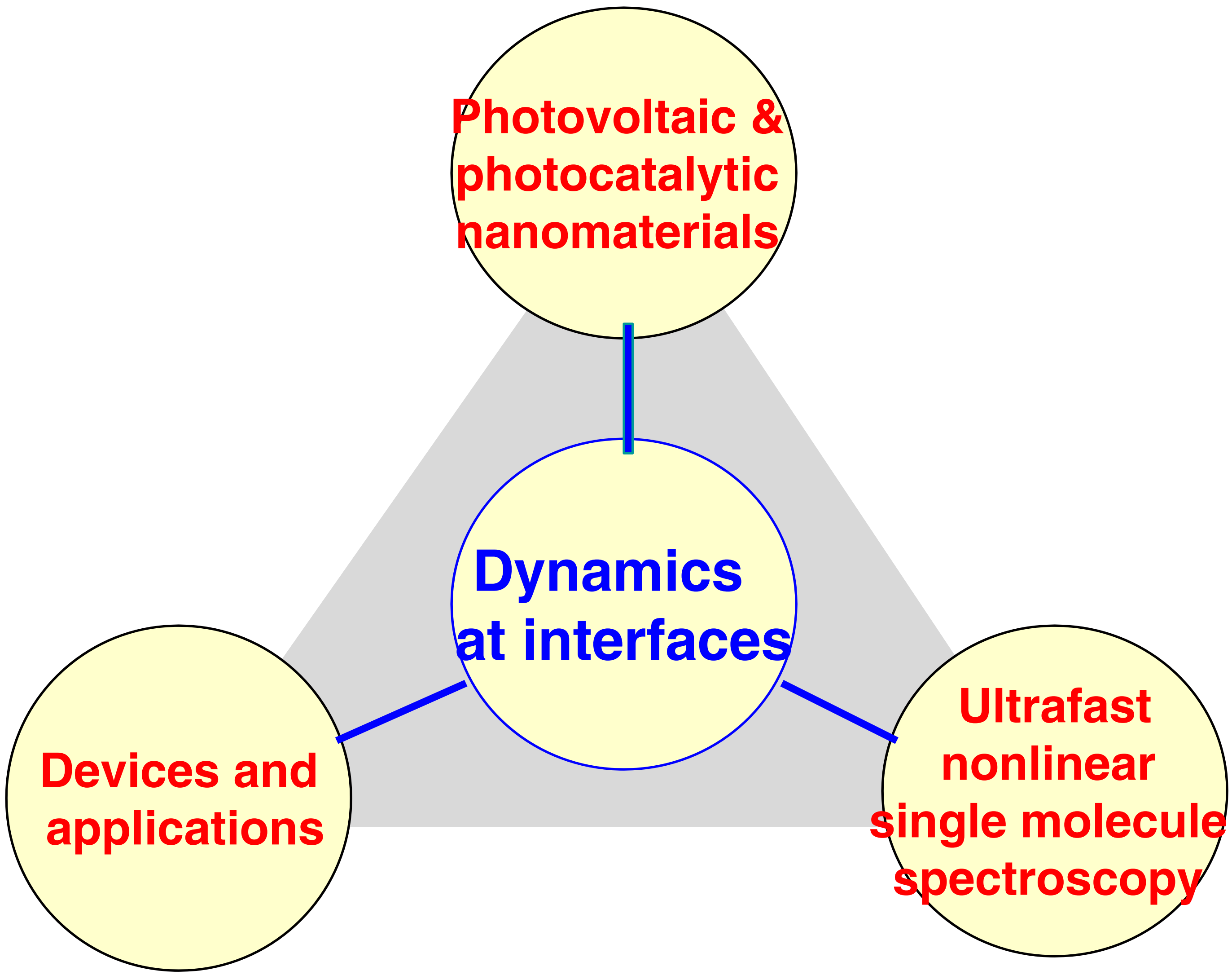
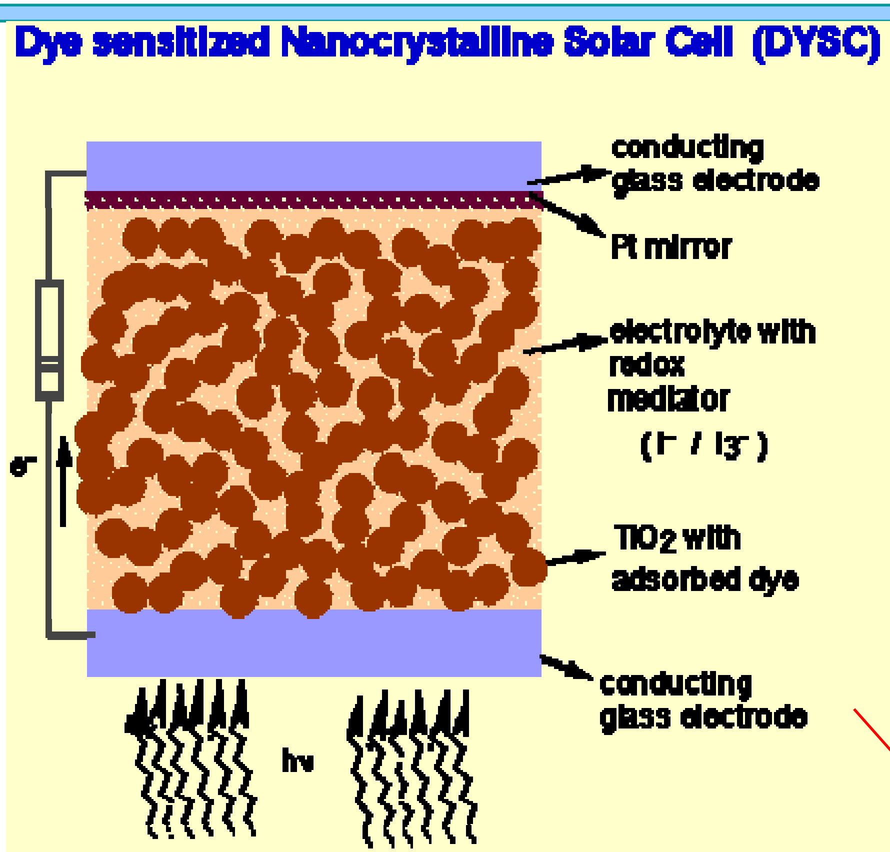
Department of Chemistry
Emory University

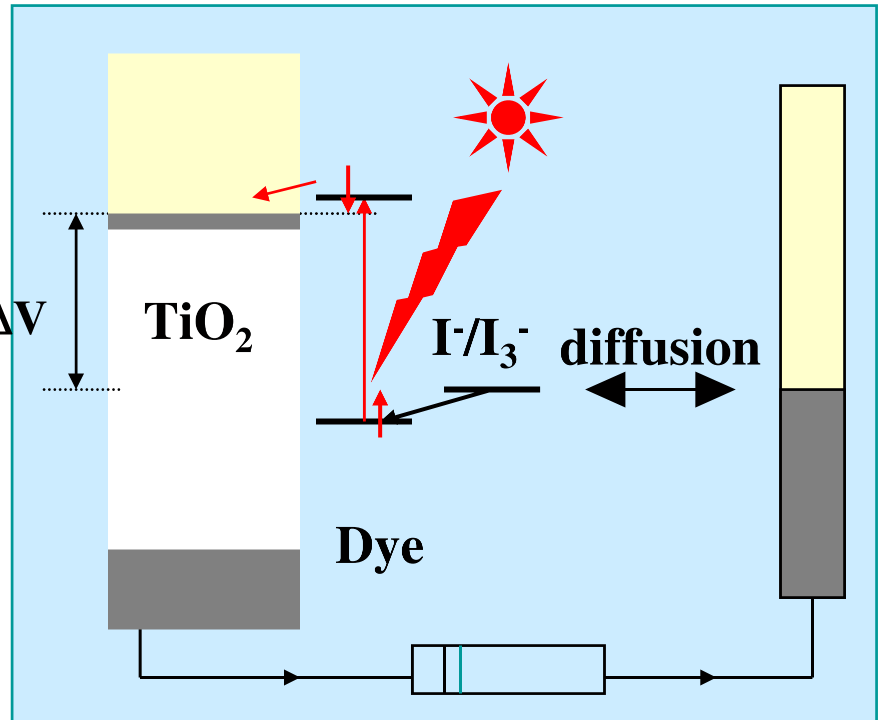
Research Interests

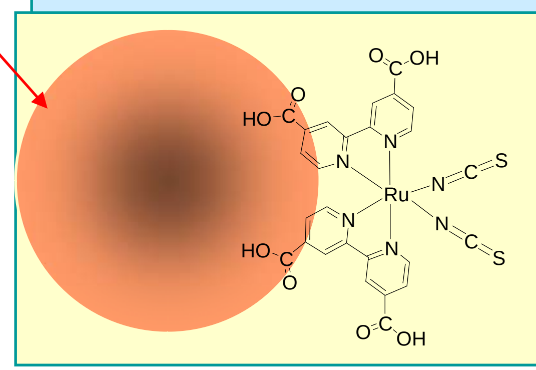
Solar energy conversion using nanomaterials



Dye-sensitized nano-crystalline semiconductor thin film solar cell





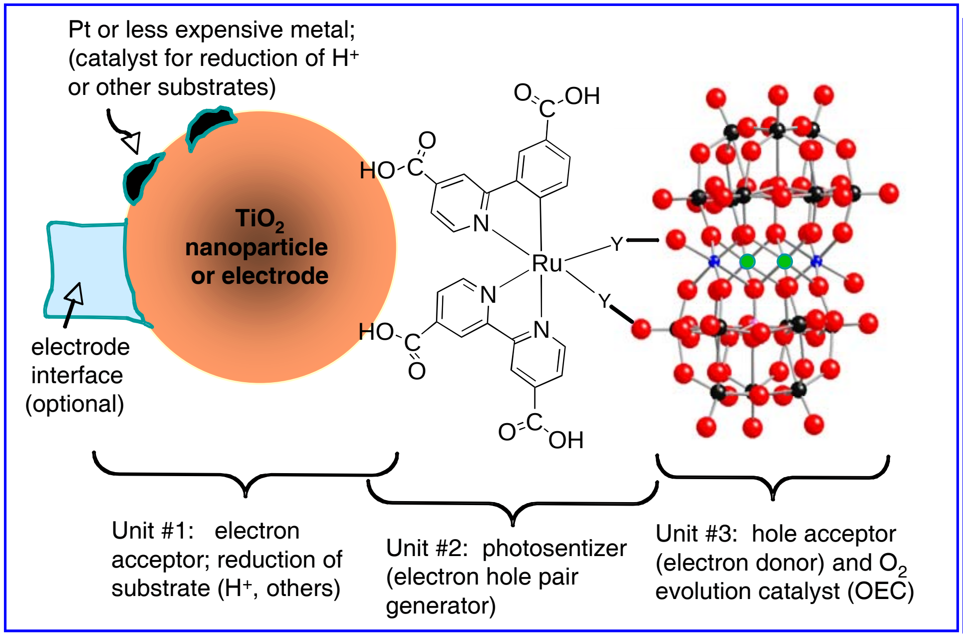


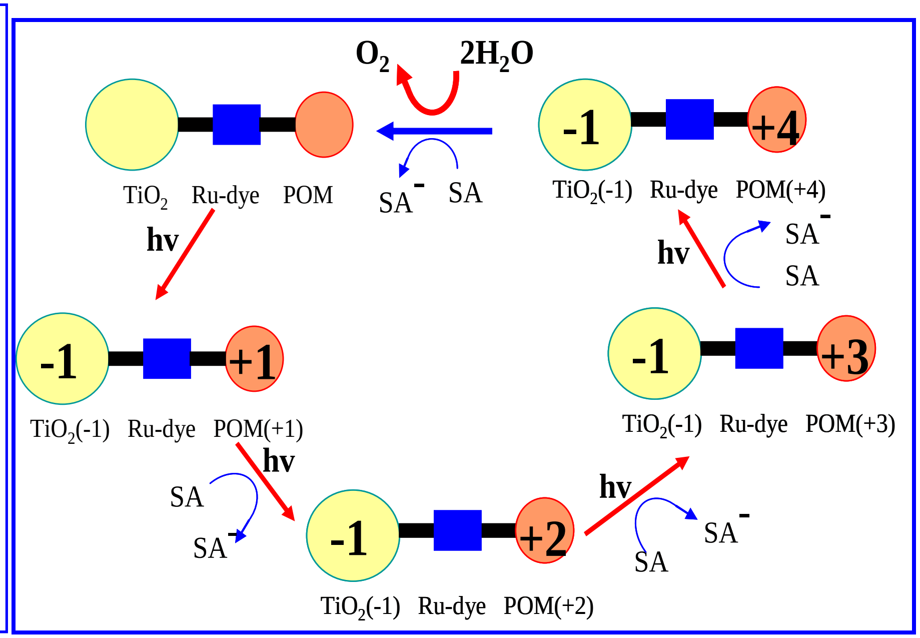
~10% solar-electric conversion efficiency
http://dcwww.epfl.ch/icp/ICP-2/solarcellE
O'Regan, Gratzel, Nature, 1991, 353, 737.
Bach, Gratzel et. al. Nature, 1998, 395, 583

Controlling interfacial ET is crucial in nanomaterials-based solar cells

Solar energy-driven robust multi-electron-transfer catalysts for O_2 evolution

Joint project with Craig Hill and Jamal Musaev

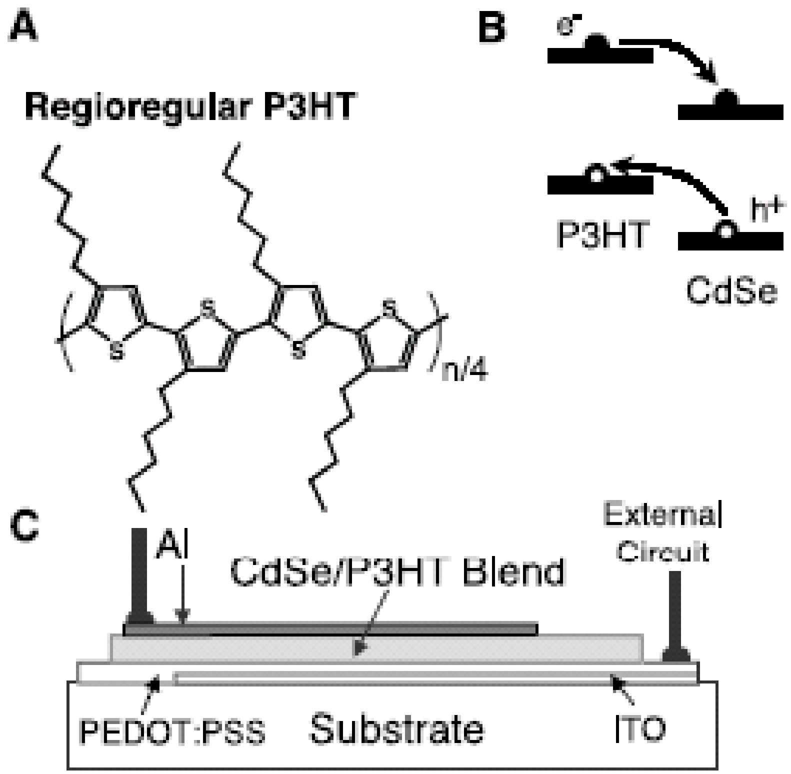


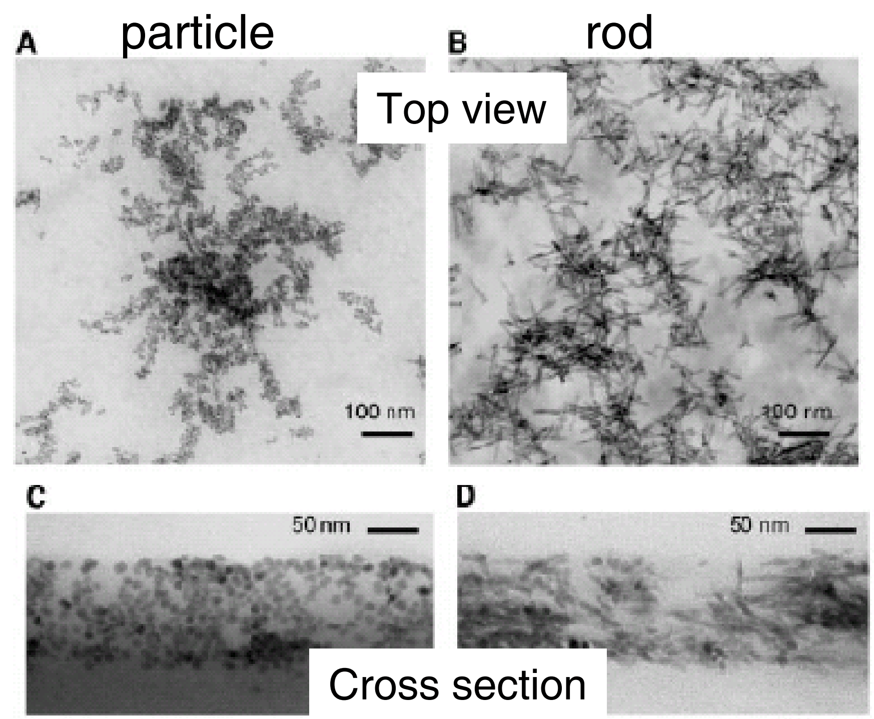


Rational:

- Three component nano-assembly approach
- O_2 evolution catalyst: robust di-Ru (or multi-Mn) poly-oxometalate (POM)
- Light harvesting: Ru-polypyridyl (known sensitizer)
- Photo-oxidation: Dye-sensitized TiO_2 (proven long lived charge separation)

Nanocomposite thin film solar cell
(Nanorod/Conjugated polymer)



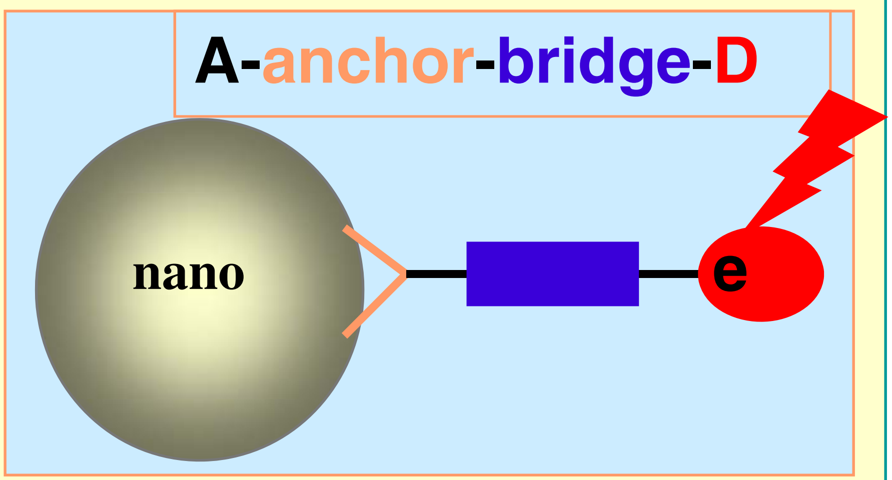


Paul Alivisatos group (efficiency: 1.7%)
SCIENCE VOL 295 (2002) 2425

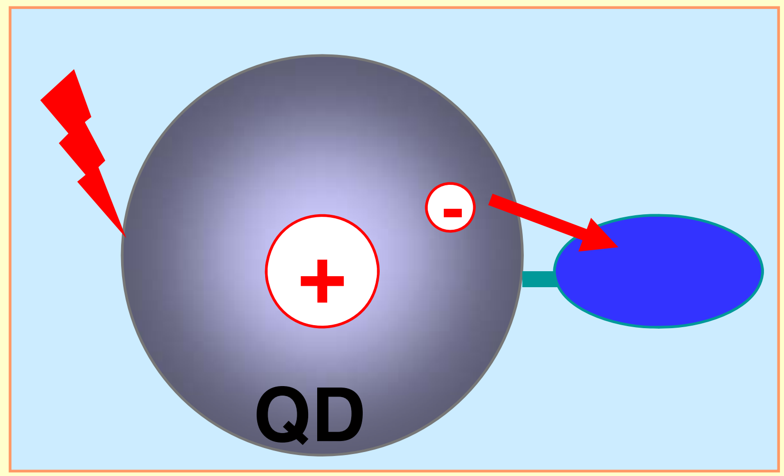
Charge separation: close contact of polymer and nanorod
Charge transport: interconnected networks of polymers(for holes)
and particles (for electrons)

Controlling interfacial ET is crucial in nanomaterials-based solar cells

I
Electron Transfer to Nanoparticles: Semiconductor Dependence

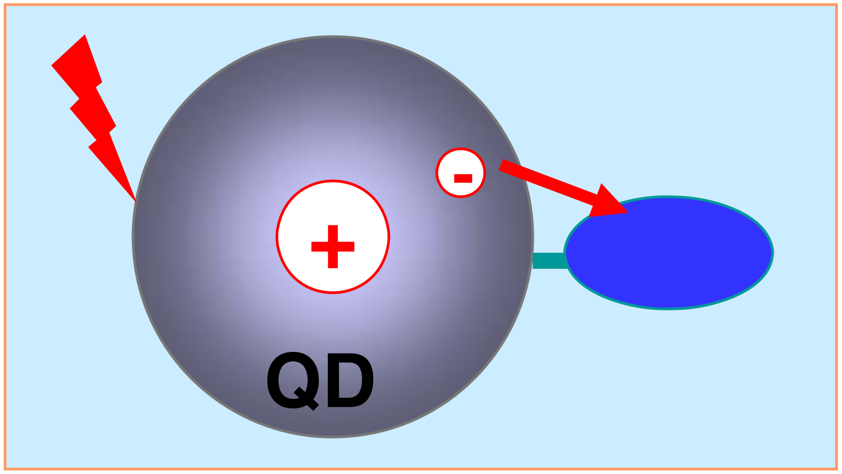


II
Electron Transfer from Quantum Dots – Towards Multiexciton Dissociation



J. Phys. Chem. B (feature) 2001, 105, 4545
Coordination Chemistry Review, (2004) 248, 1231
Annual Review of Physical Chemistry, (2005) 56, 491

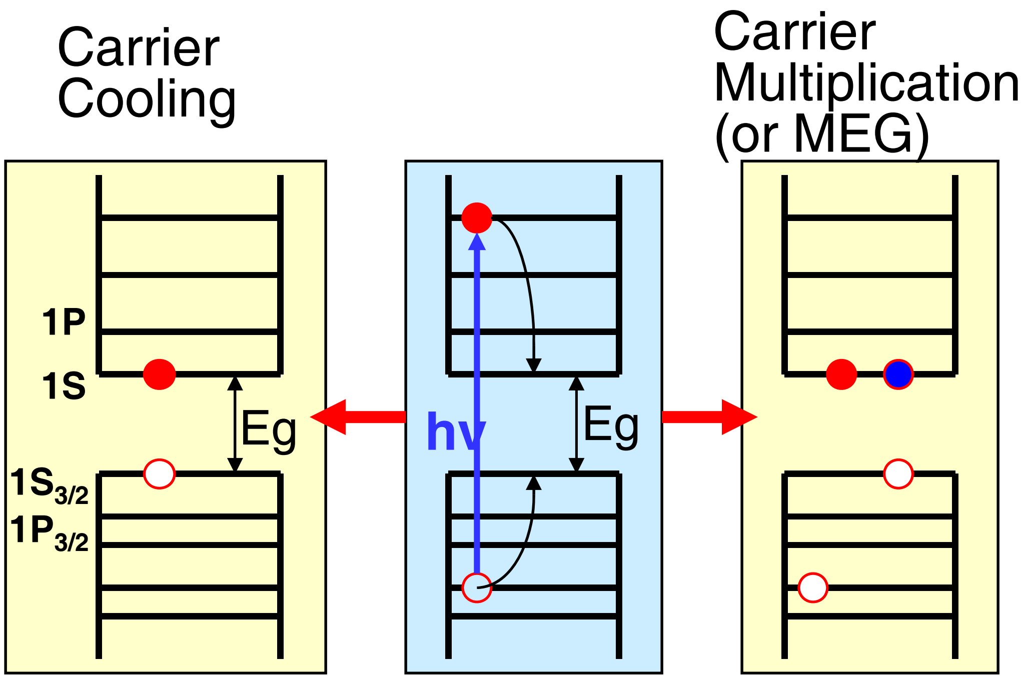
Outline



- Introduction-Multi-Exciton Generation
- Exciton dissociation pathway in CdS/RhB
- Size dependence in CdS/RhB
- Multiexciton dissociation in CdSe/RhB
- Single QD electron transfer

Multi-Exciton Generation (MEG)

Multiple-Exciton Generation by ONE absorbed photon



Effect of quantum confinement on:
Carrier relaxation
Exciton interaction (Annihilation and MEG)

MEG has been reported in:
CdSe, PbSe, PbS, PbTe, InAs, Si

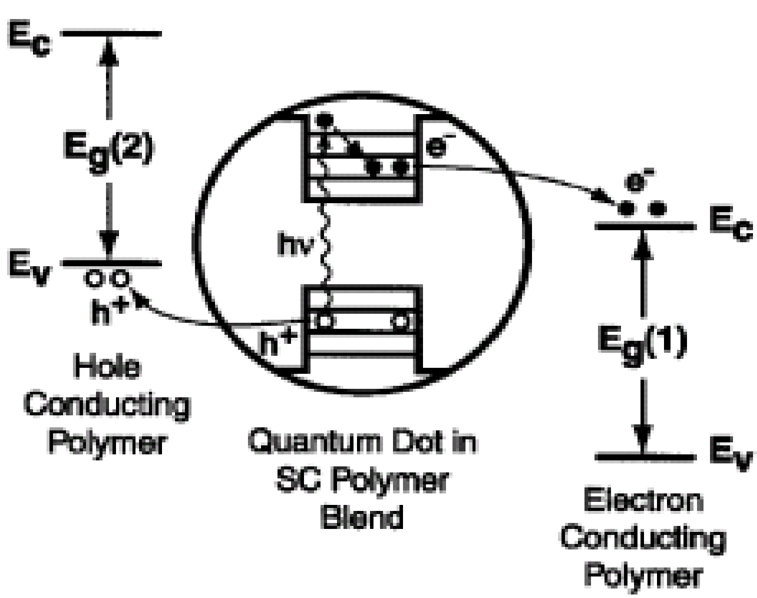
Klimov
2004, PbSe: 2 excitons (PRL, 92, 186601)
2006: PbSe: 7 excitons (NanoLett, 6, 424)
2006: CdSe: (JPC B 110, 25332)
Nozik:
2005: PbSe, PbS (Nano Lett, 5, 865)
2006: PbTe (JACS, 128, 3241)
2007: PbSe film (Nano Lett, 7, 1779)
2007: Si (Nano Lett, 2007)
Bonn, Banin, Ruhman
2007: InAs (JPC C, 111,4146)
Prasad: (2008) (APL, 92, 031107)
PbSe photoconductor

MEG has been disputed:
Bawendi et al., PRB, 76, 081304R (2007)
Bonn, Banin, Ruhman, NL, (2008),8,1207

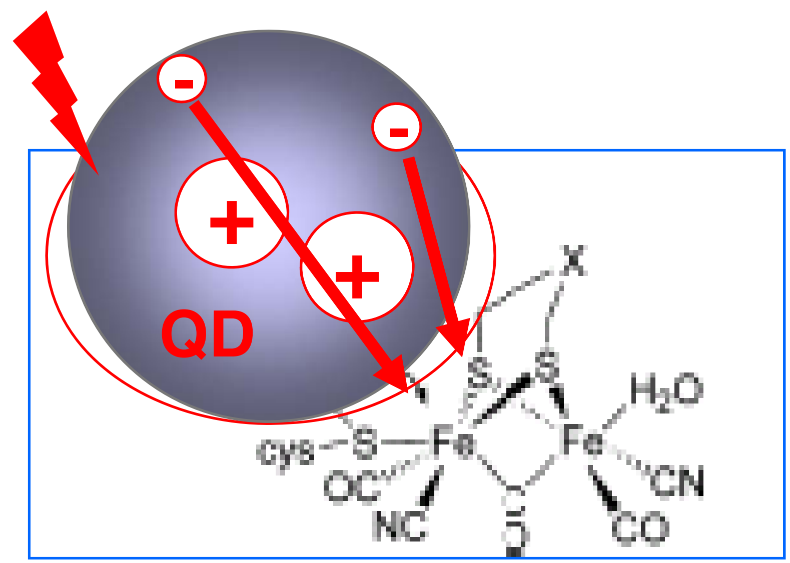
Applications of Multi-Exciton Generation

•Quantum Dot Solar Cells

Nozik, Physica E, 14, (2002), 115

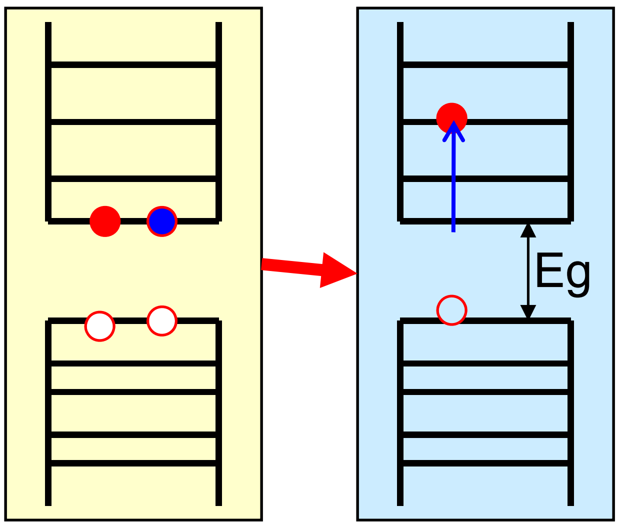


•Multi e/h-redox center for catalysis

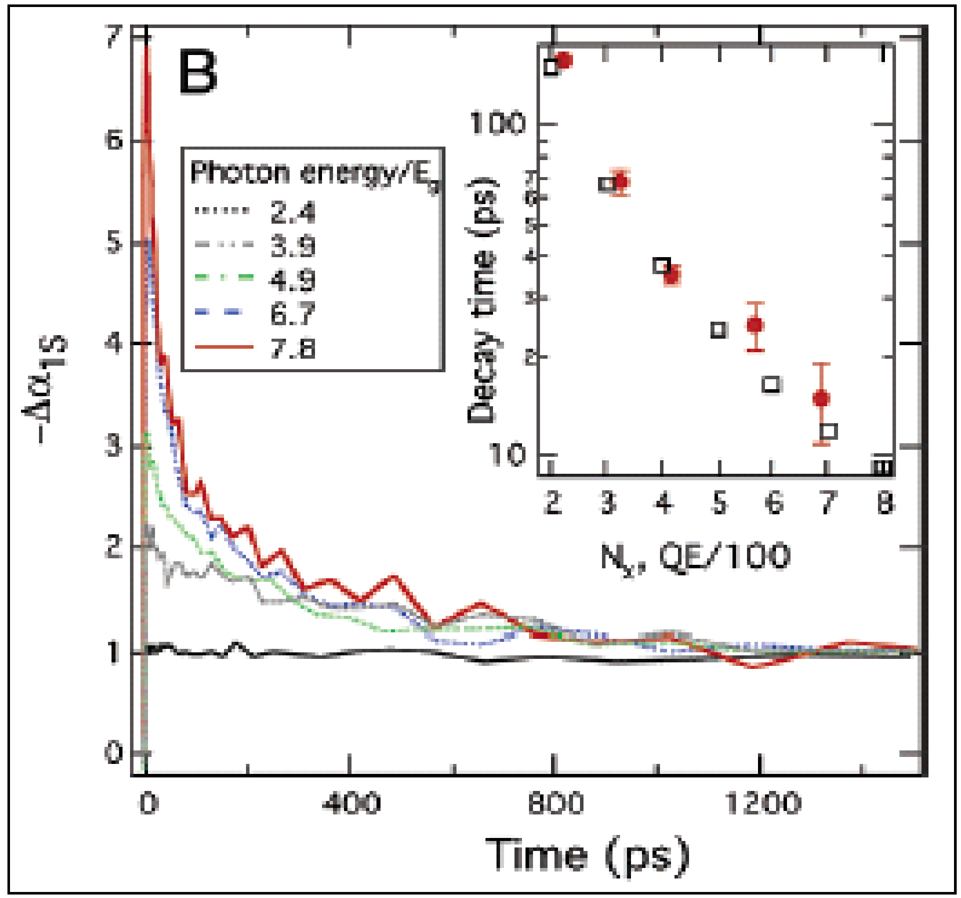


With Stefan Lutz

Challenges in Using MEG

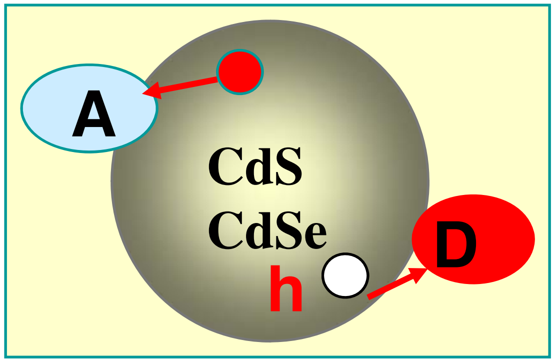


Exciton-Exciton annihilation: ~10 – 100 ps



Klimov et al, Nano Letters, 2006, 6, 424:
PbSe, Seven excitons

Challenges in Using MEG
- Ultrafast Interfacial Charge Separation

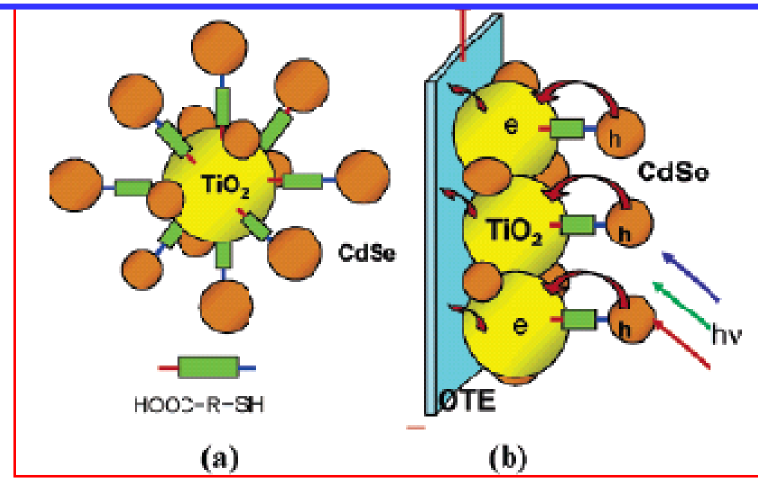


Henglein, Brus, Gratzel, Kamat,….

El-Sayed: ET CdS to MV^{2+}: 300 fs
(*J. Phys. Chem. A* 1998, *102*, 5652)
CdSe/benzoquinone: e->ads ->hole shuttling ~3ps
(*J. Phys. Chem. B* 1999, *103,* 1783)

Kamat: CdSe-Phenylenediamine hole transfer
(*J. Phys. Chem. B* **2003,** *107,* 10088)

Klimov: CdSe/Rudye: hole transfer ~5ps
(JACS 128, 2006, 9985.)



Kamat et al. J. AM. CHEM. SOC. 2006, 128, **2385**

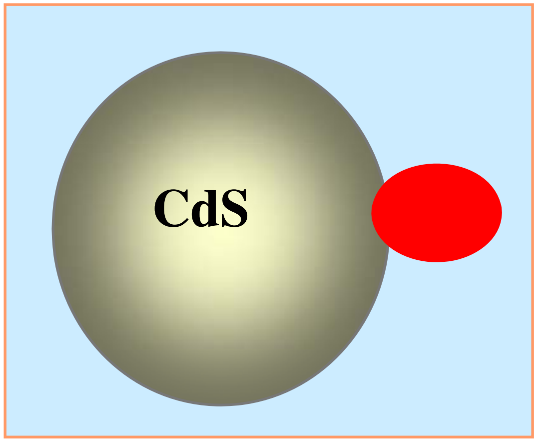
Kamat: ET CdSe -> TiO_2: 5 -100 ps

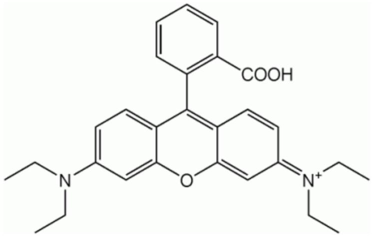
Nozik:

- ET from CdSe to TiO_2: 10 -50 ps
(*J. Phys. Chem. B* **2003,** *107,* 14154)
- InP/TiO_2:
hole transfer to adsorbate: ~4ps
ET to TiO_2: trap mediated
(*J. Phys. Chem. B* **2005,** *109,* 2625)

• How to achieve ultrafast multi-exciton dissociation?

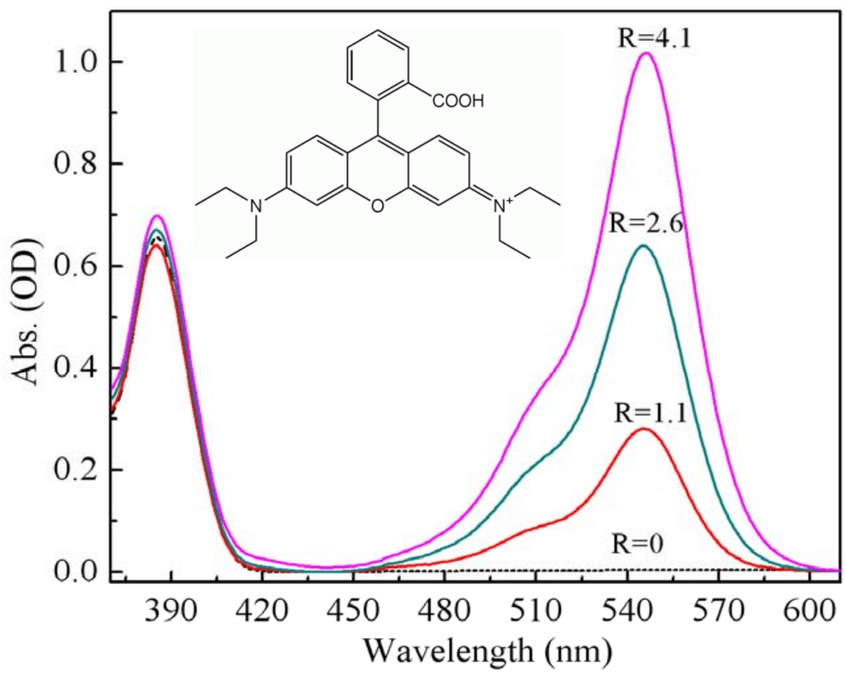
Outline

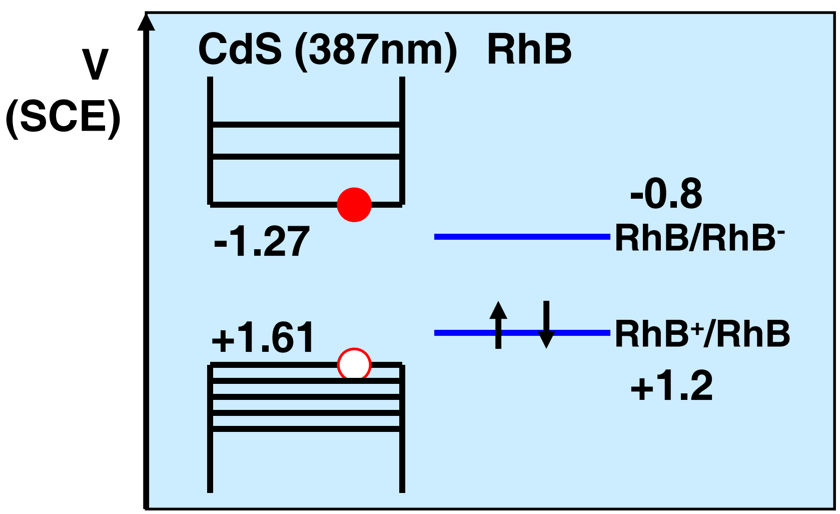


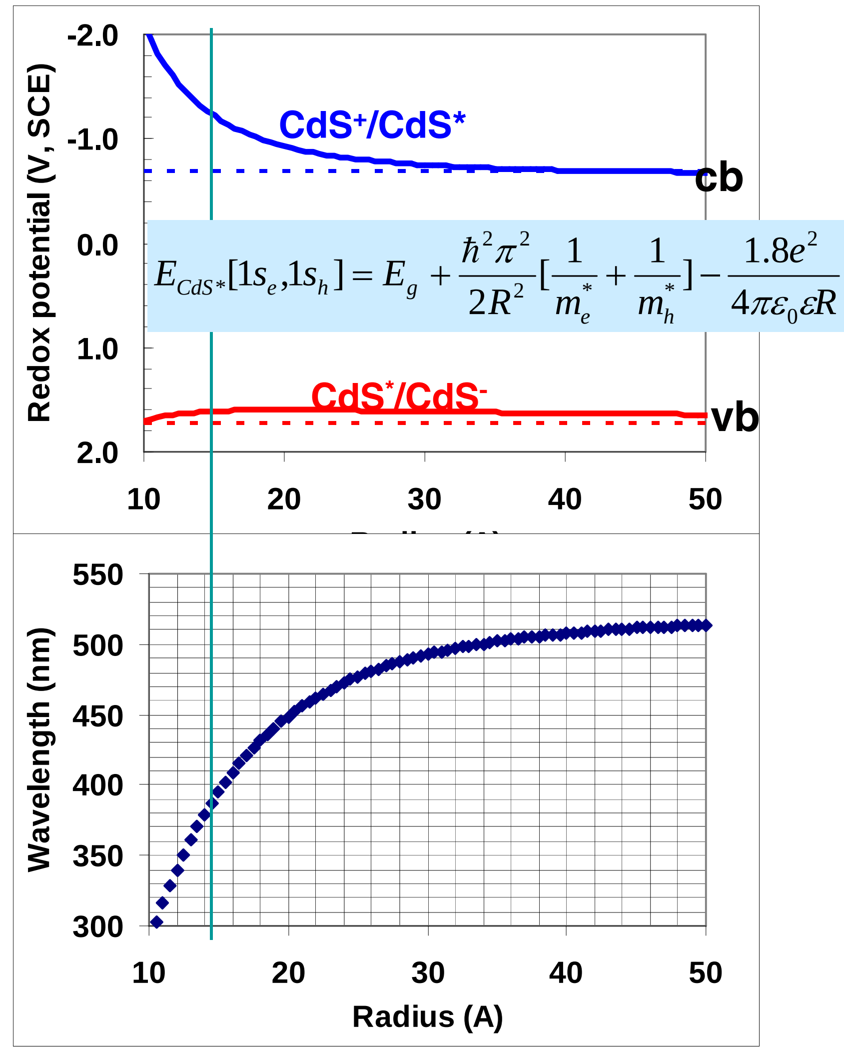


- Introduction-Multiexciton Generation
- **Exciton dissociation pathway in CdS/RhB**
- Size dependence in CdS/RhB
- Multiexciton dissociation in CdSe/RhB
- Single particle electron transfer

CdS-RhB: Spectra and Energetics



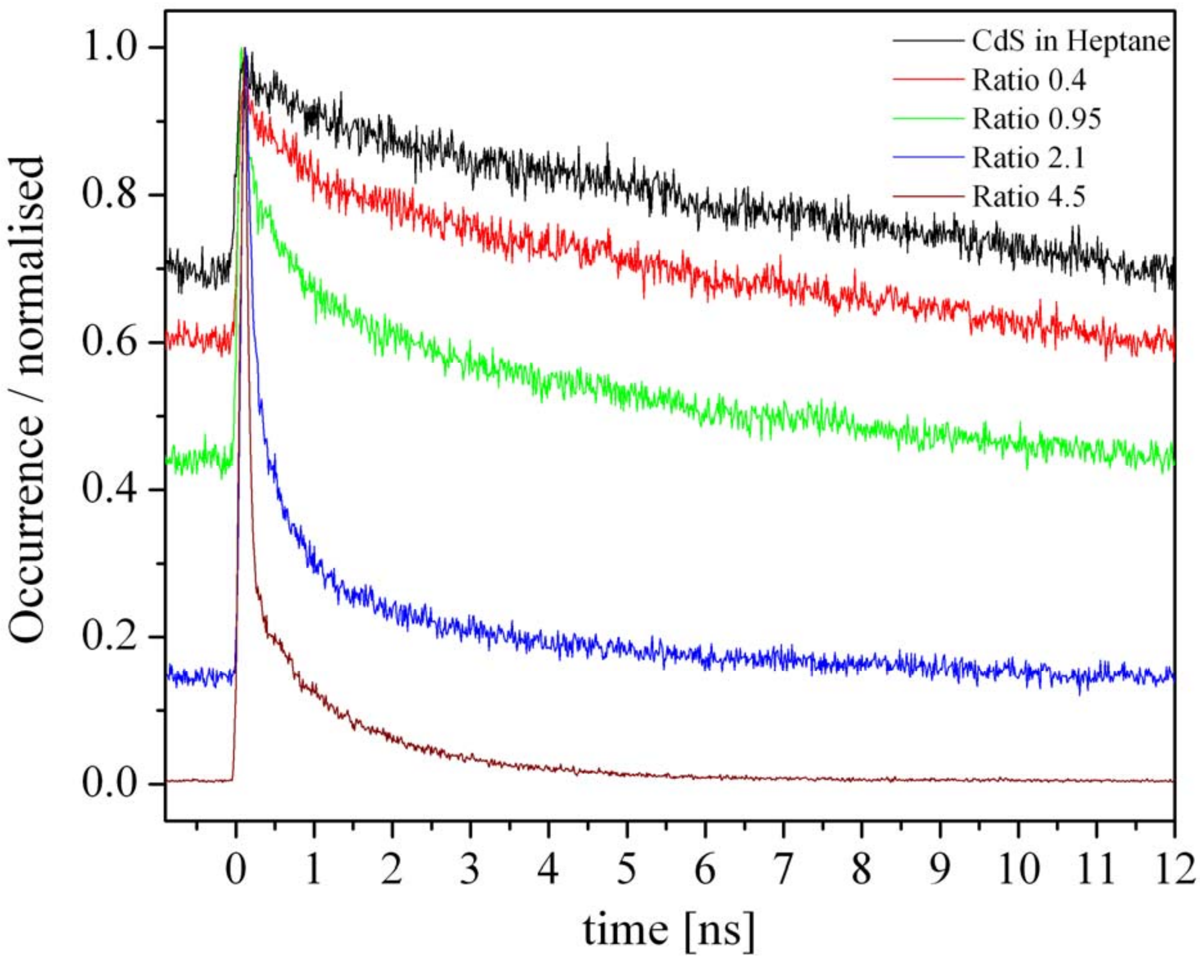


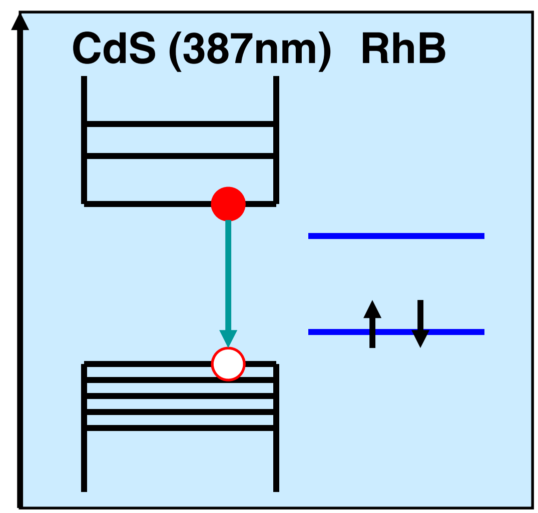


QD: Brus, L. E., . *J. Chem. Phys.* **1984, 80,** 4403.
J. Chem. Phys. **1983, 79,** 5566.

RhB: Fisher et al, J. Photochem., 1985, 30, 475

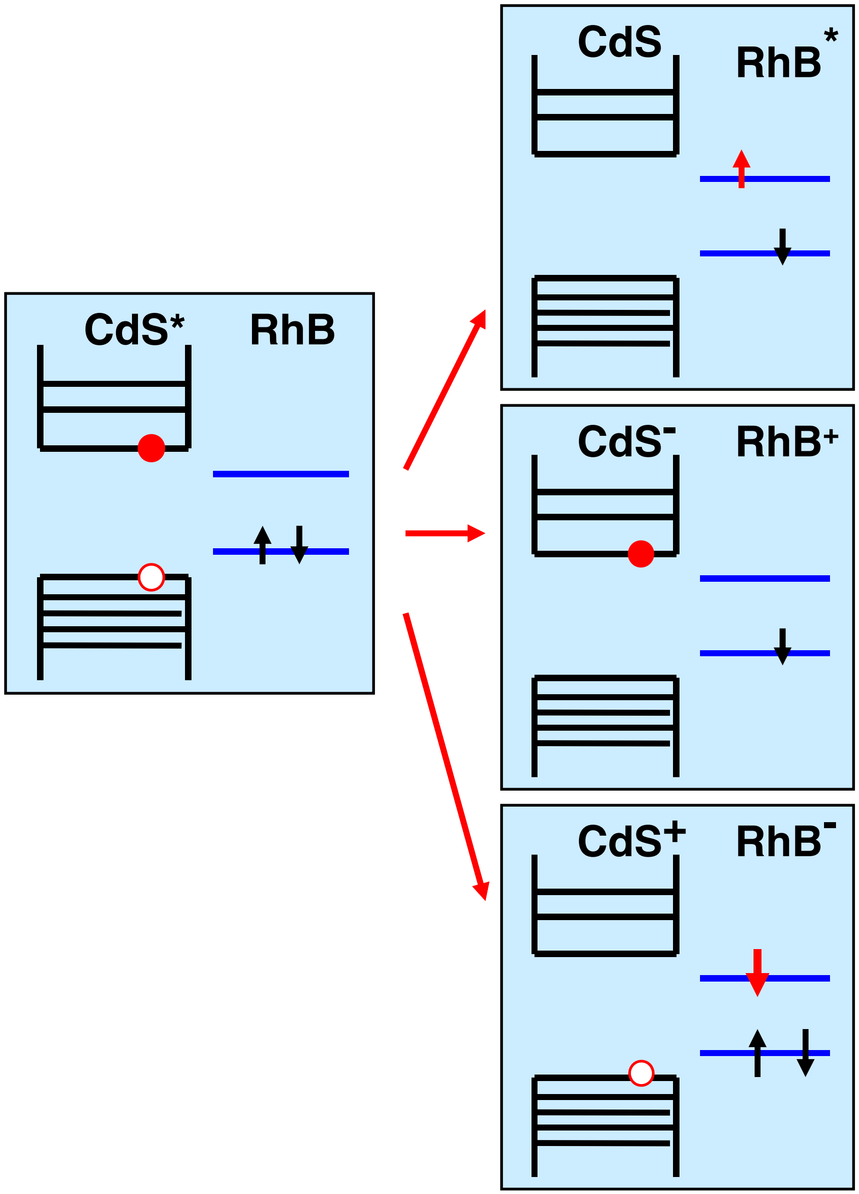
Fluorescence Lifetime of CdS in CdS/ RhB





- CdS emission (415-450) is quenched by RhB
- quenching rate increases with the # of RhB

Possible Exciton quenching Pathways



1) Energy Transfer

$$CdS*[1s_e,1s_h]+RhB \rightarrow CdS + RhB*$$

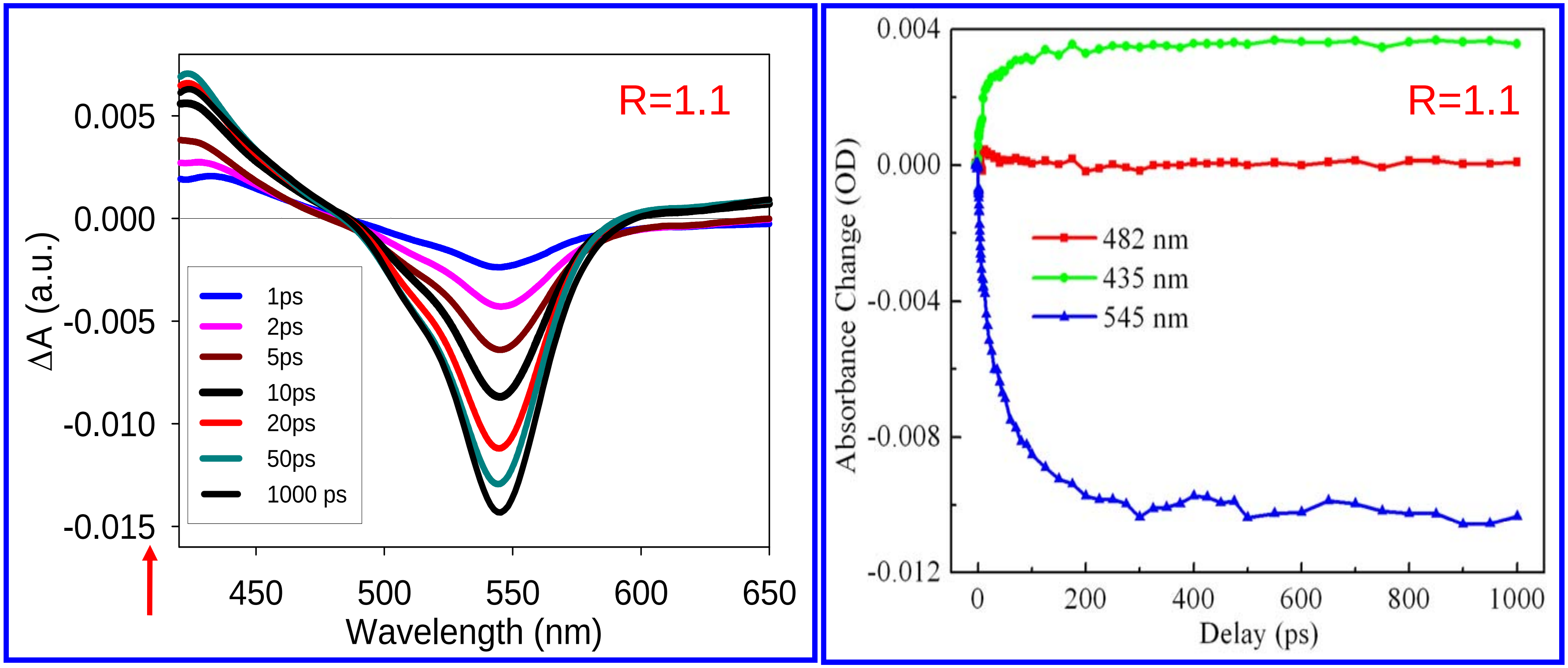
2) Hole Transfer

$$CdS*[1s_e,1s_h]+RhB \rightarrow CdS^-[1s_e]+RhB^+$$

3) Electron Transfer

$$CdS*[1s_e,1s_h]+RhB \rightarrow CdS^+[1s_h]+RhB^-$$

Transient spectra of CdS/RhB



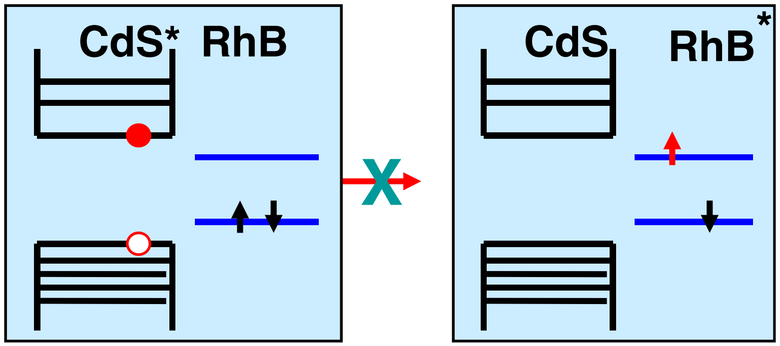
Excitation wavelength: 400 nm: CdS

- **Bleach of RhB ground state absorption**
- **Formation of a new specie at ~420nm (same kinetics as bleach)**
- **Clear isosbestic point at 482nm**

Possible exciton quenching pathways

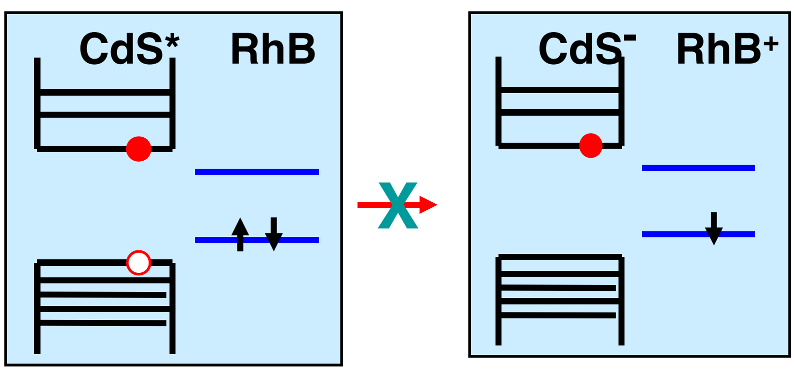
1) Energy Transfer

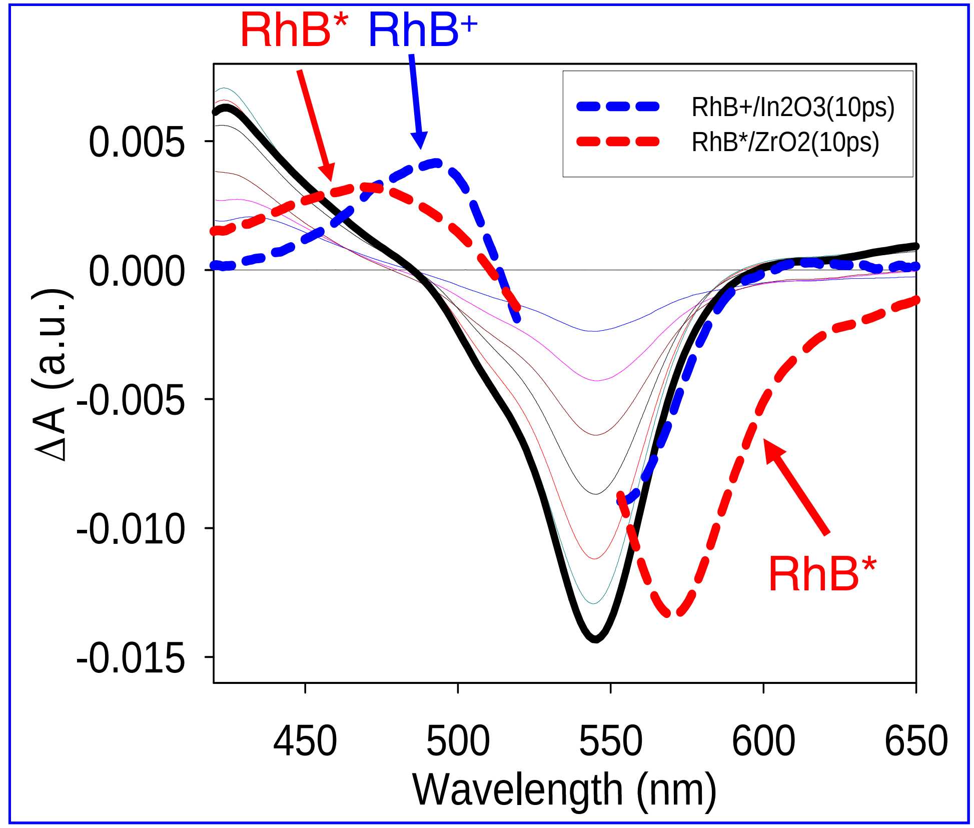
$$CdS^*[1s_e, 1s_h] + RhB \rightarrow CdS + RhB^*$$

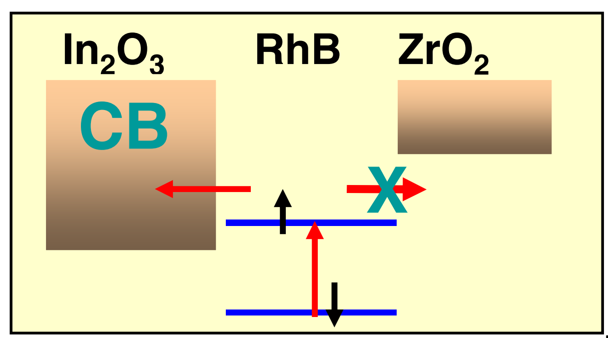


2) Hole Transfer

$$CdS^*[1s_e, 1s_h] + RhB \rightarrow CdS^-[1s_e] + RhB^+$$





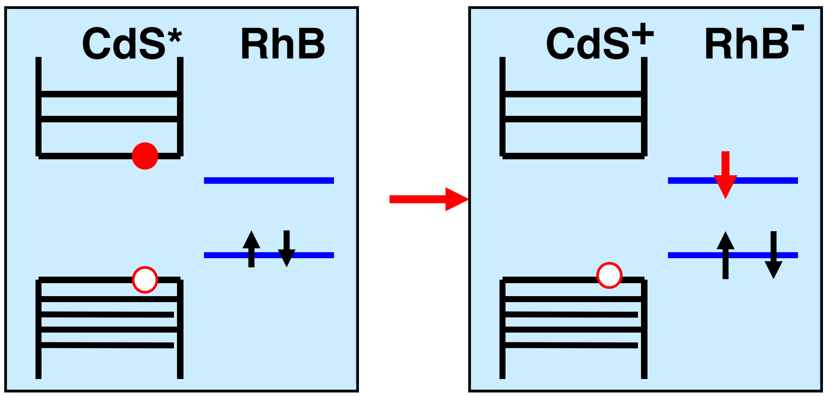


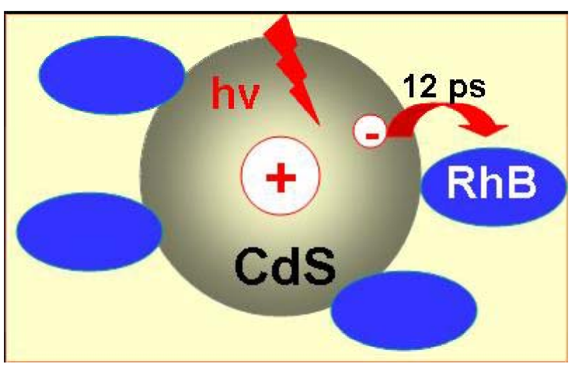
JPCC (2008), 112, 5203

Possible Exciton Quenching Pathways

3) Electron Transfer

$$CdS^*[1s_e,1s_h] + RhB \rightarrow CdS^+[1s_h] + RhB^-$$





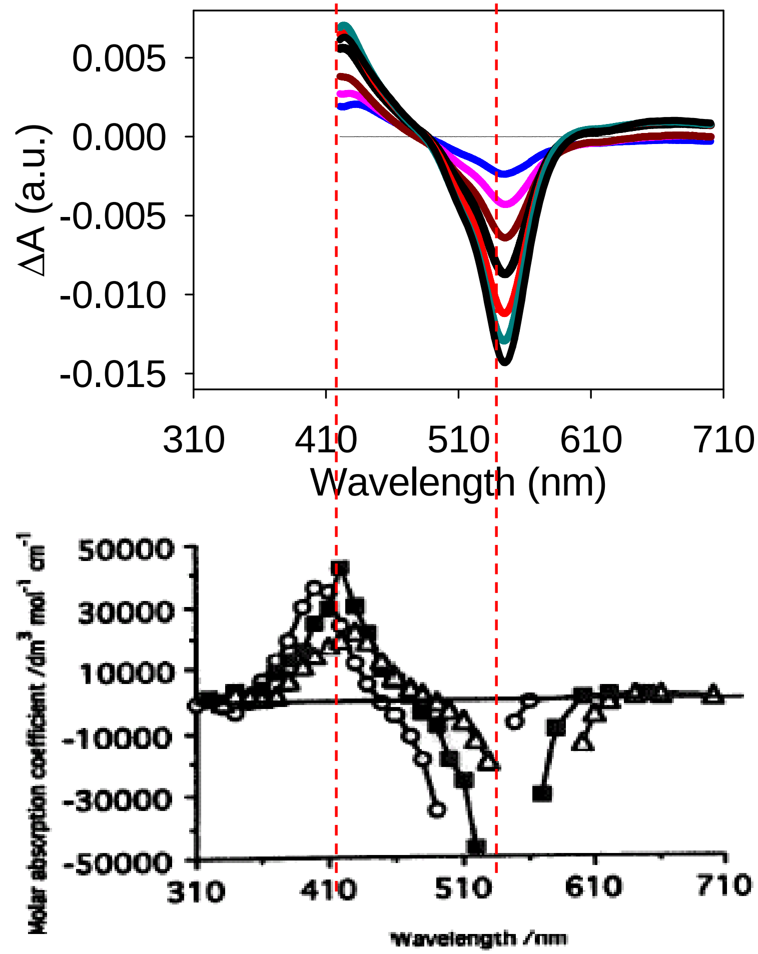
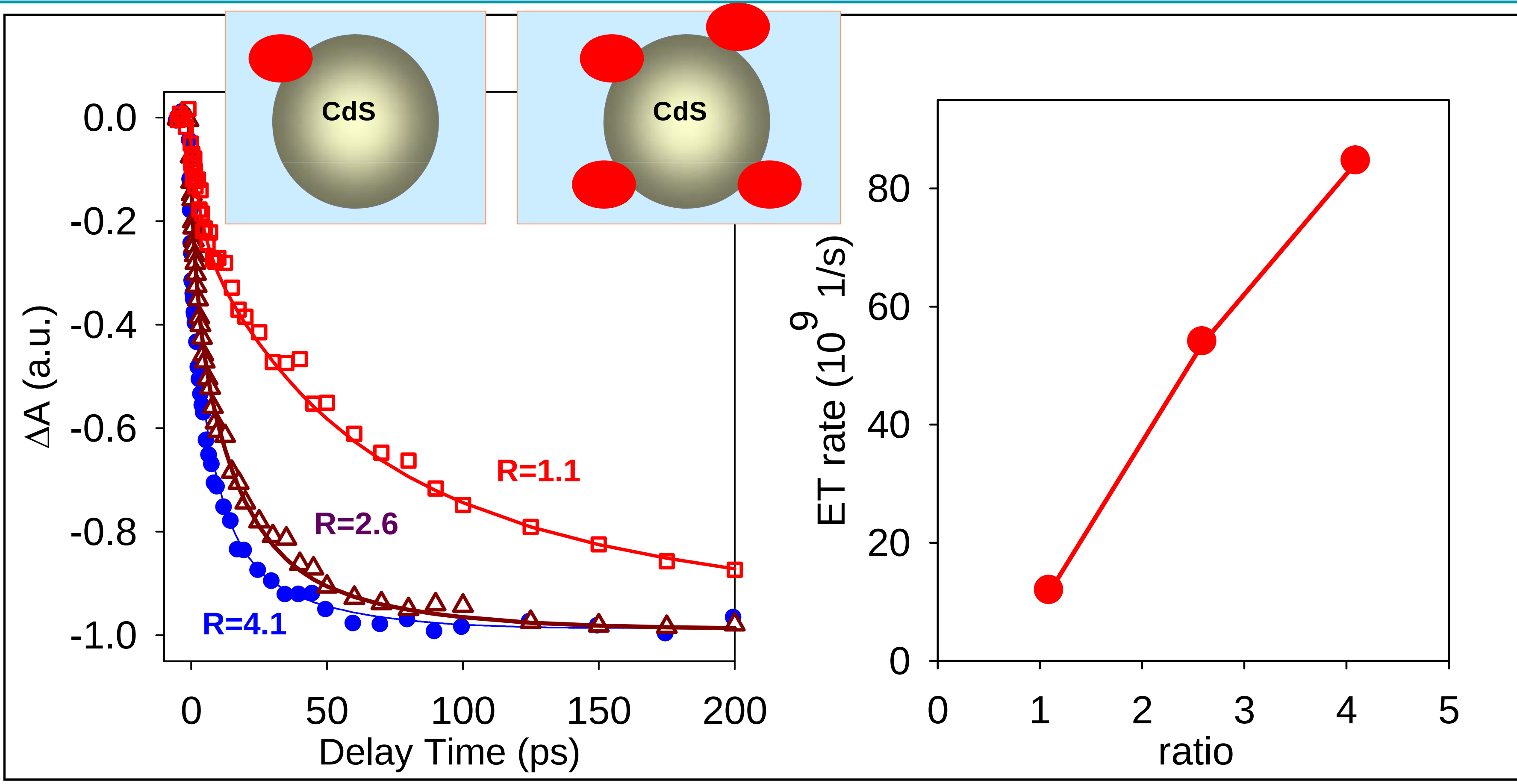


Fig. 13. Transient absorption spectra observed on pulse radiolysis of nitrogen saturated aqueous solutions (pH 7) of rhodamine dye (2×10^{-5}) mol dm^{-3}) containing 0.1 mol dm^{-3} *t*-butanol (○, rhodamine 6G; ■, rhodamine B; △, rhodamine 101 (all 20 μs measured after the pulse).

Journal of Photochemistry and Photobiology A: Chemistry **1997, 107, 175.**

Dependence of ET rate on CdS/RhB ratio

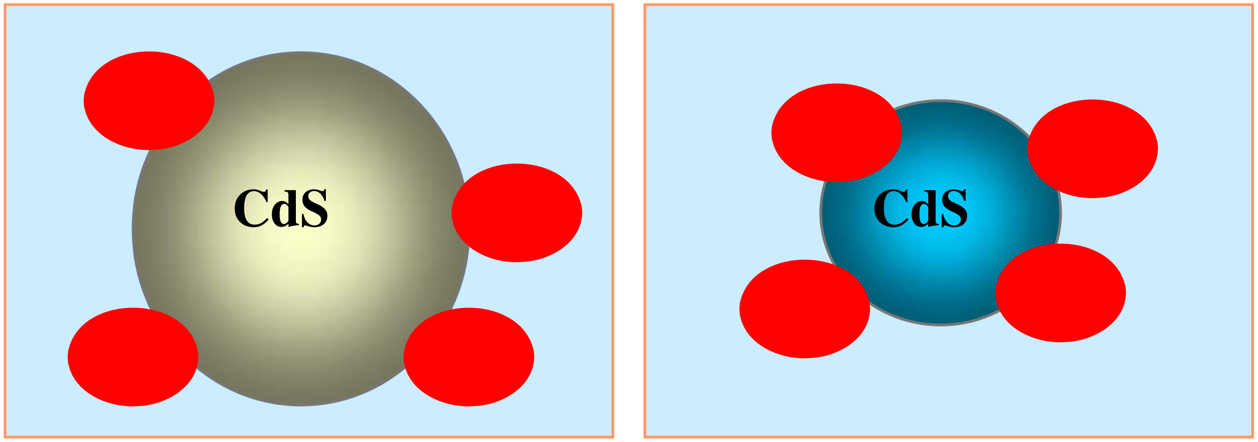


- ET rate increases with # of adsorbate
- at ~4 RhB/CdS, ET rate ~1/10ps

--- similar to/faster than exciton-exciton quenching rate

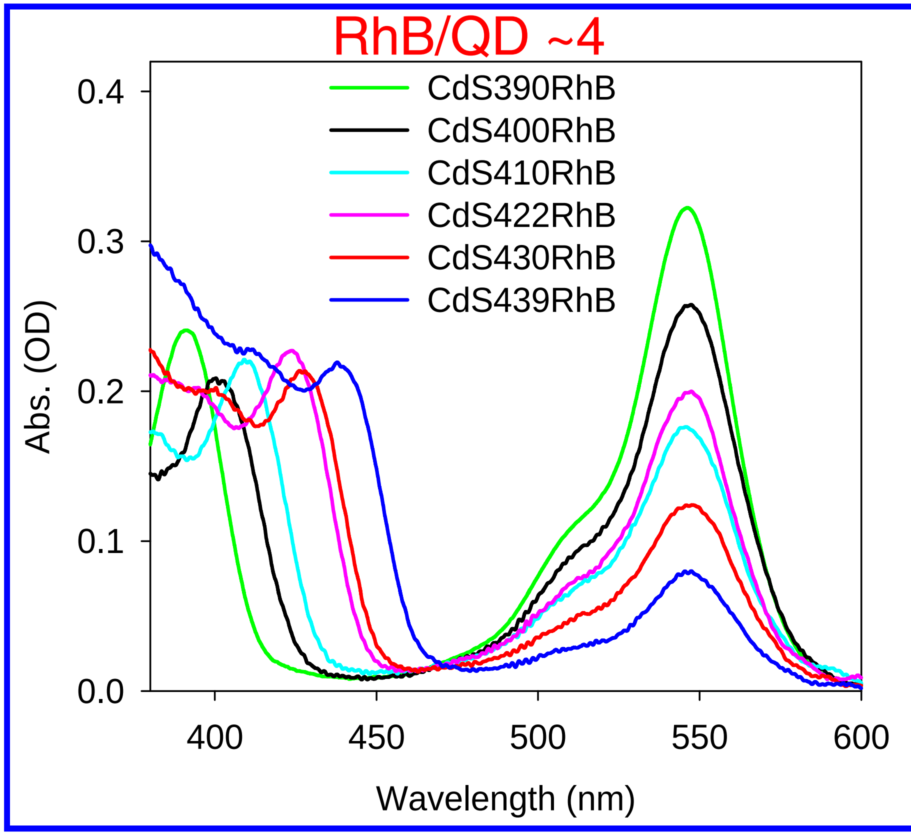
J. AM. CHEM. SOC. 2007, 129, 15132-15133

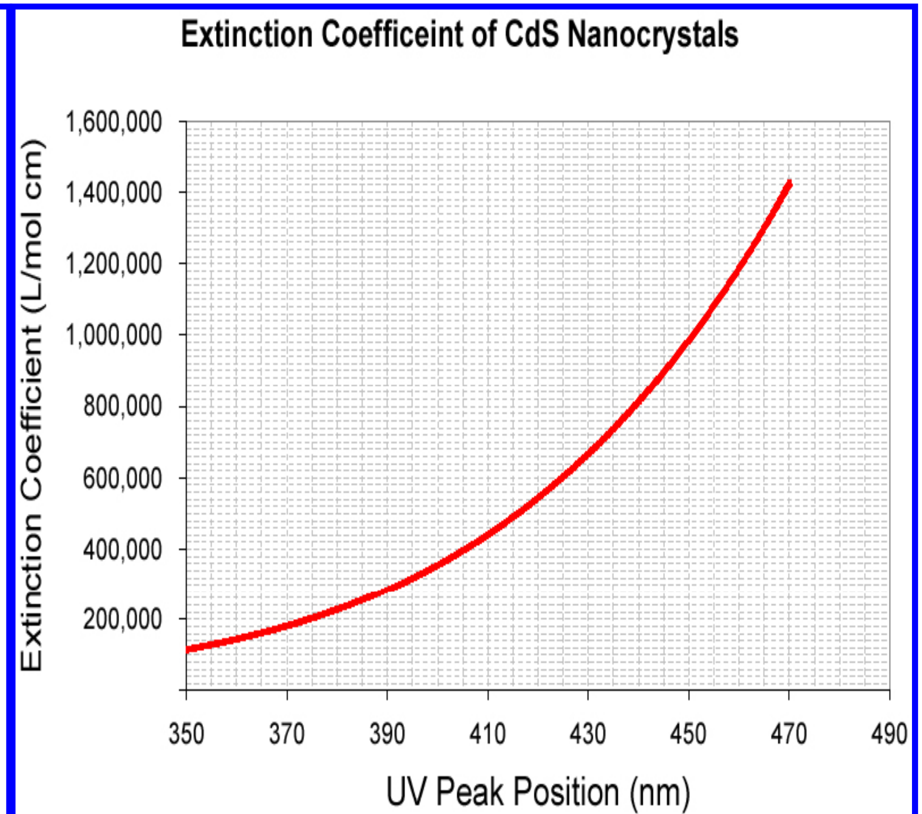
Outline



- Introduction-Multiexciton Generation
- Exciton dissociation pathway in CdS/RhB
- **Size dependence in CdS/RhB**
- multiexciton dissociation in CdSe/RhB
- Single particle electron transfer

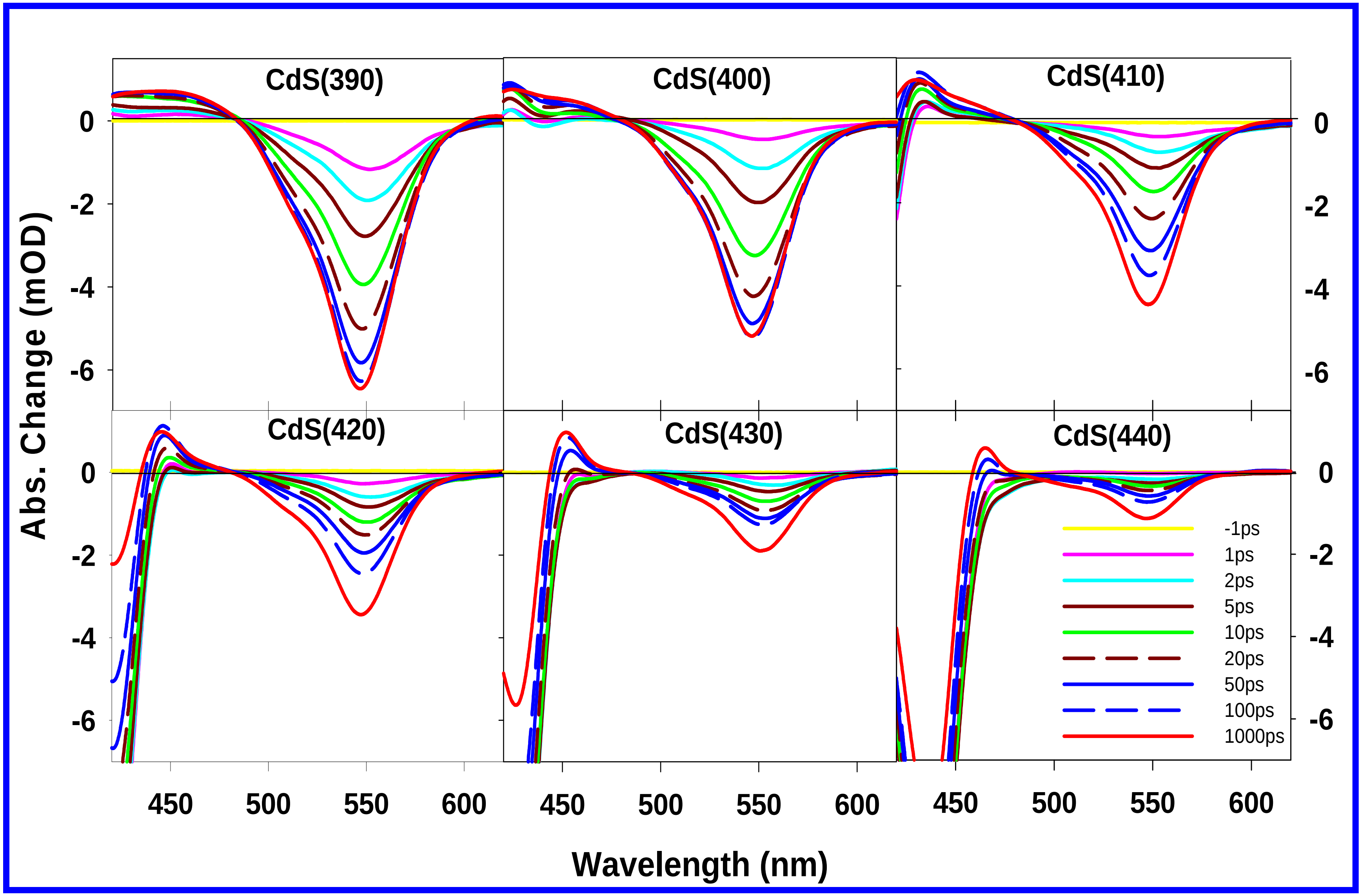
CdS/RhB Spectrum: Size dependence



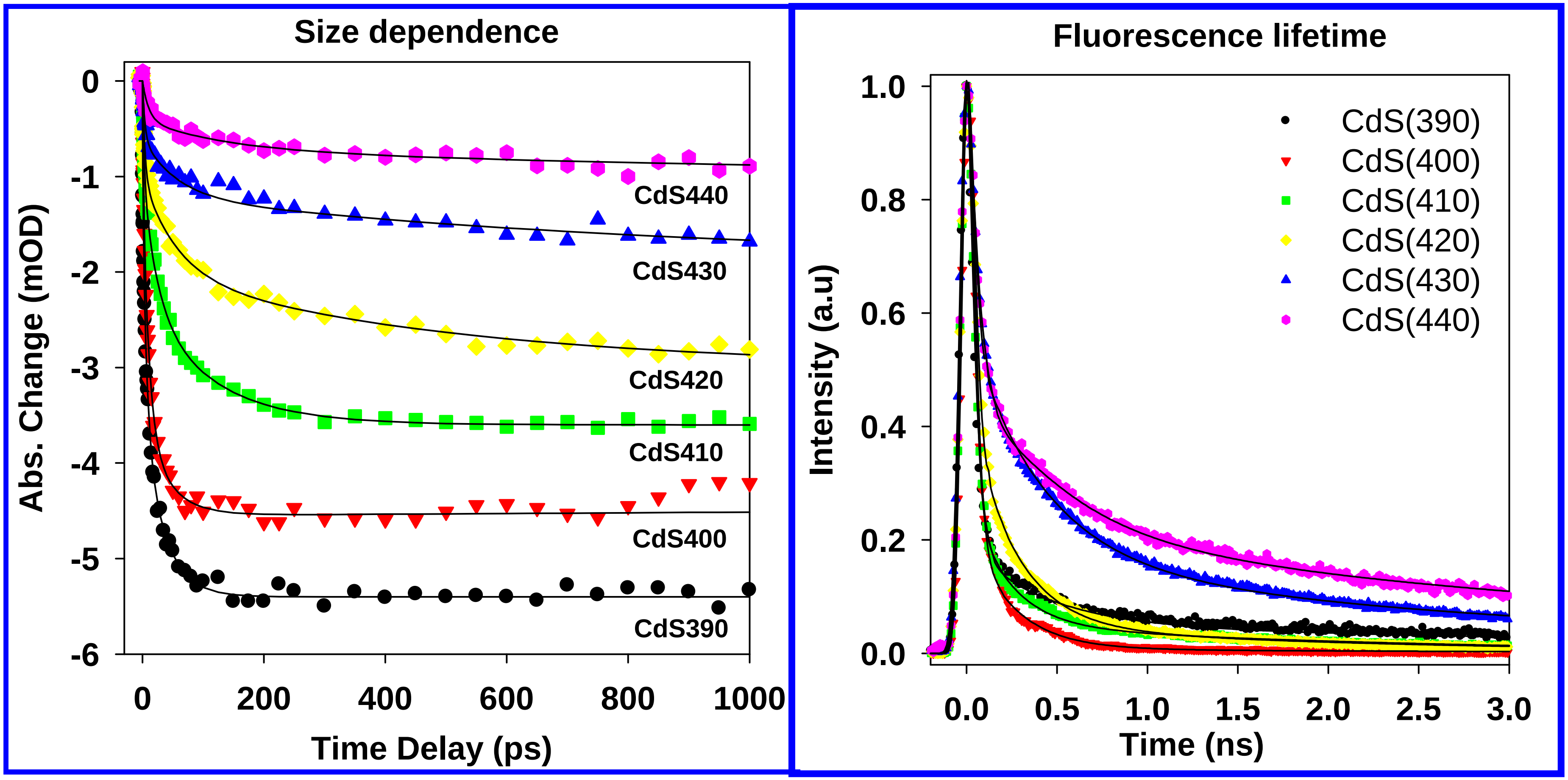


Peng, et al. *Chem. Mater.* **2003, 15, 2845.**

Dependence of ET rate on QD size

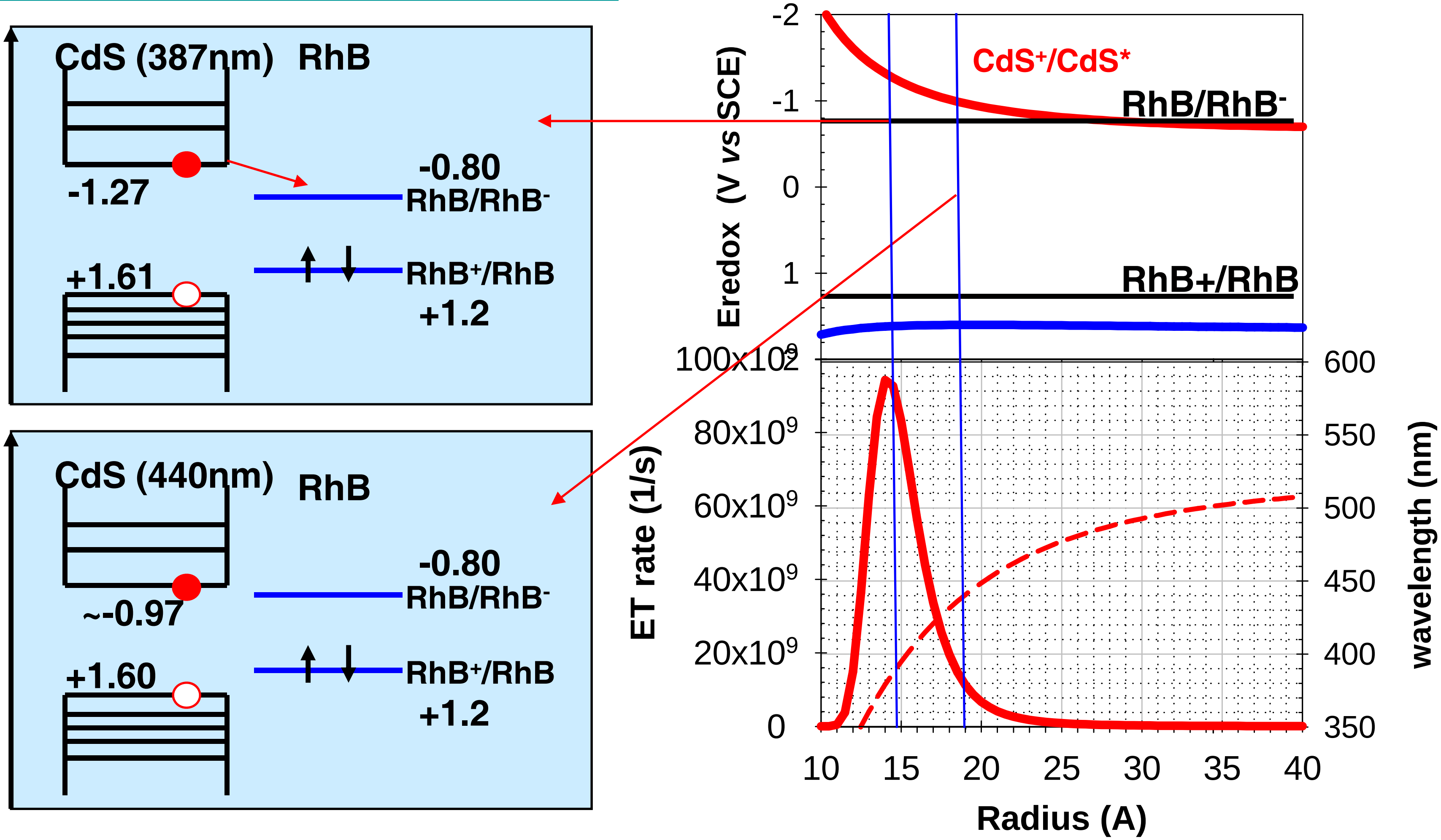


Dependence of ET rate on QD size



- Exciton dissociates by ET from CdS to RhB
- No hole transfer
- ET rate decreases at larger particle size

Origins of Size Dependence



Larger size ->

- **Less driving force for ET**
- **Reduced coupling strength?**

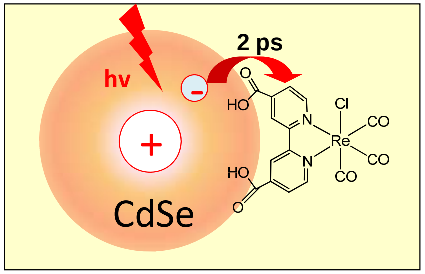
$$k(r) = \frac{2\pi}{\hbar} \frac{|H(r)|^2}{\sqrt{4\pi\lambda RT}} e^{-\frac{[-e(E_{RhB} - E_{1s}(r)) + \lambda]^2}{4\lambda RT}}$$

Why no (or much slower) hole transfer?

Interesting comparison:

CdSe/Ru(bpy)3: hole transfer ~5ps
Klimov et al JACS 128, 2006, 9985

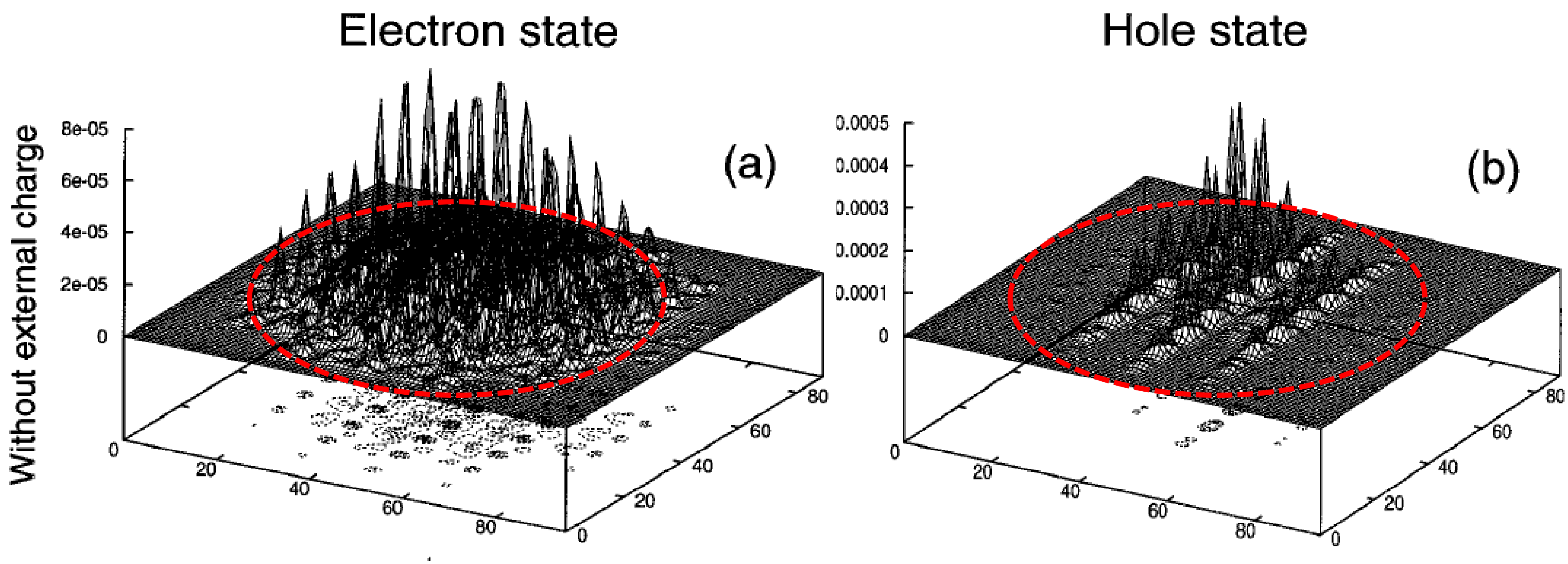
CdSe/Re(bpy)(CO)3Cl: electron transfer ~2 ps
Lian et al JACS 130, 2008, 5632



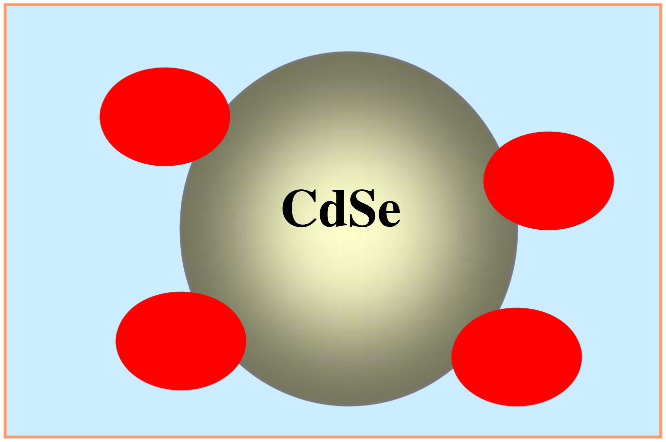
Possible reason: Different e/h amplitude on surface

Comparison of 1S electron and 1S hole

2362 *J. Phys. Chem. B, Vol. 105, No. 12, 2001* Wang



Outline



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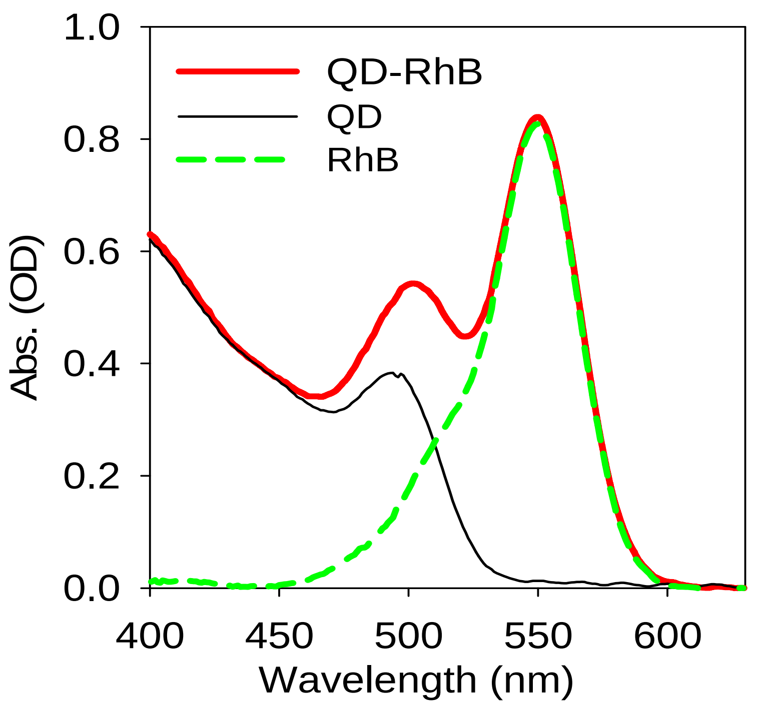
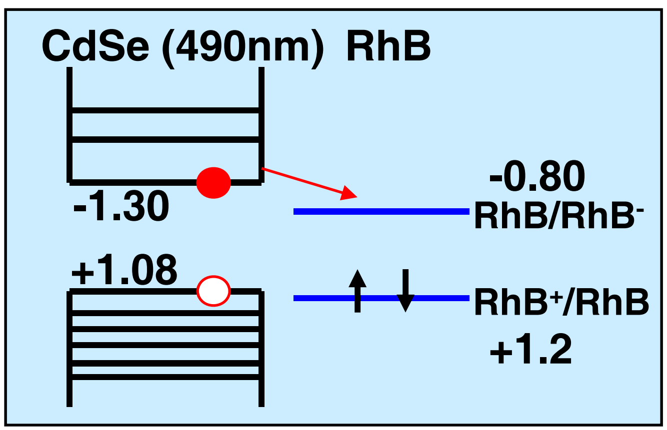
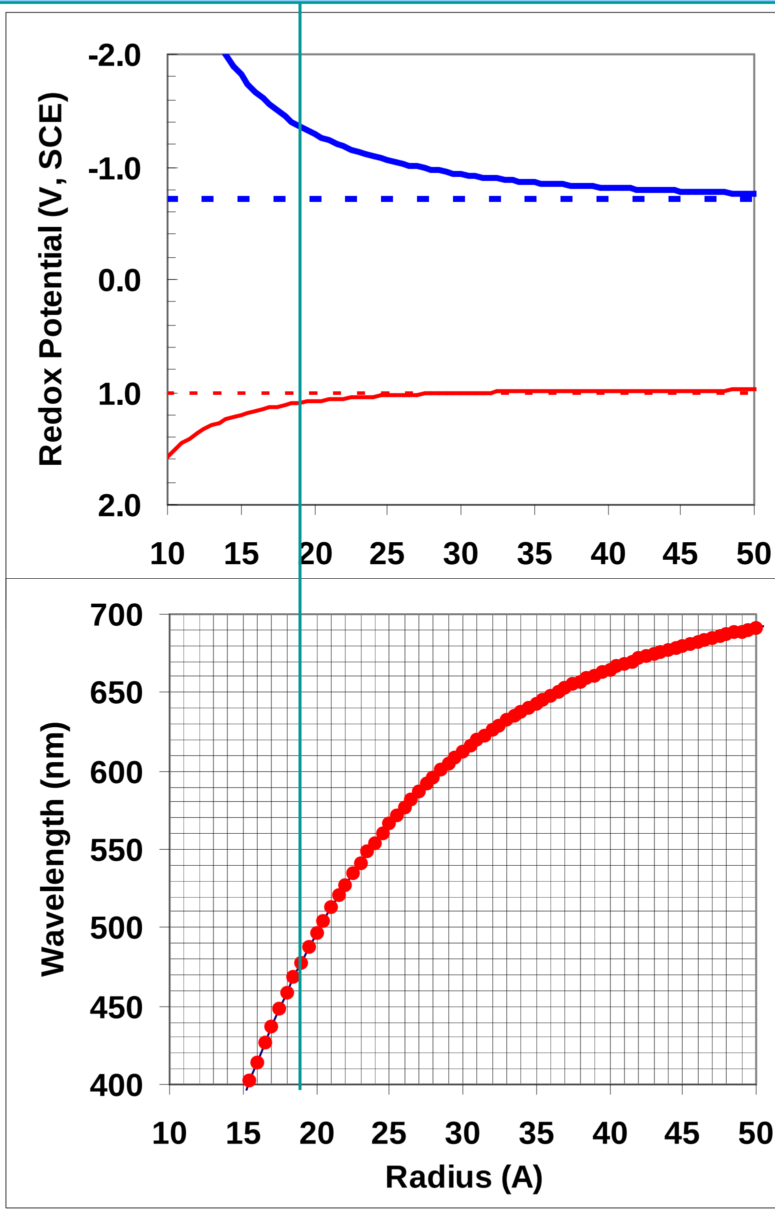
CdSe-RhB: spectrum and energetics

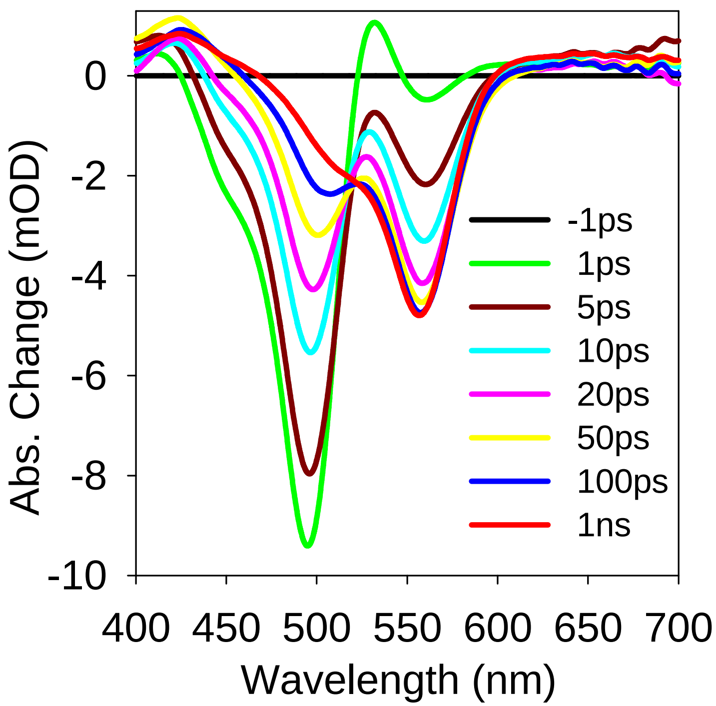


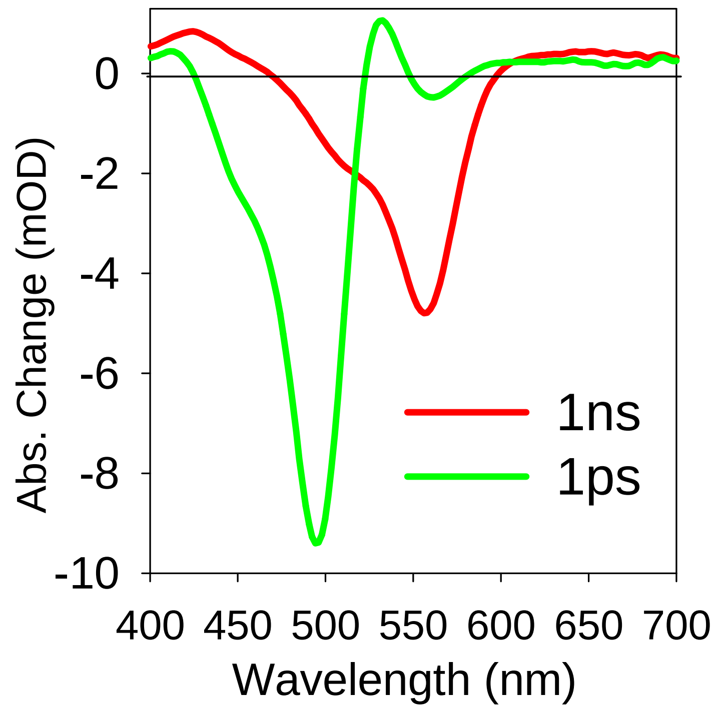




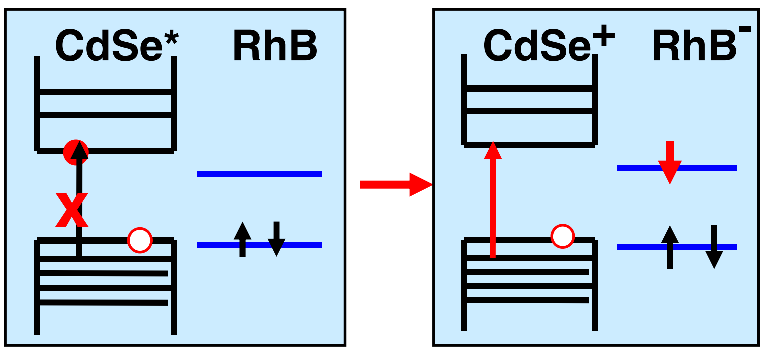
Transient Spectra of CdSe/RhB

(Pump Power 20 nJ)



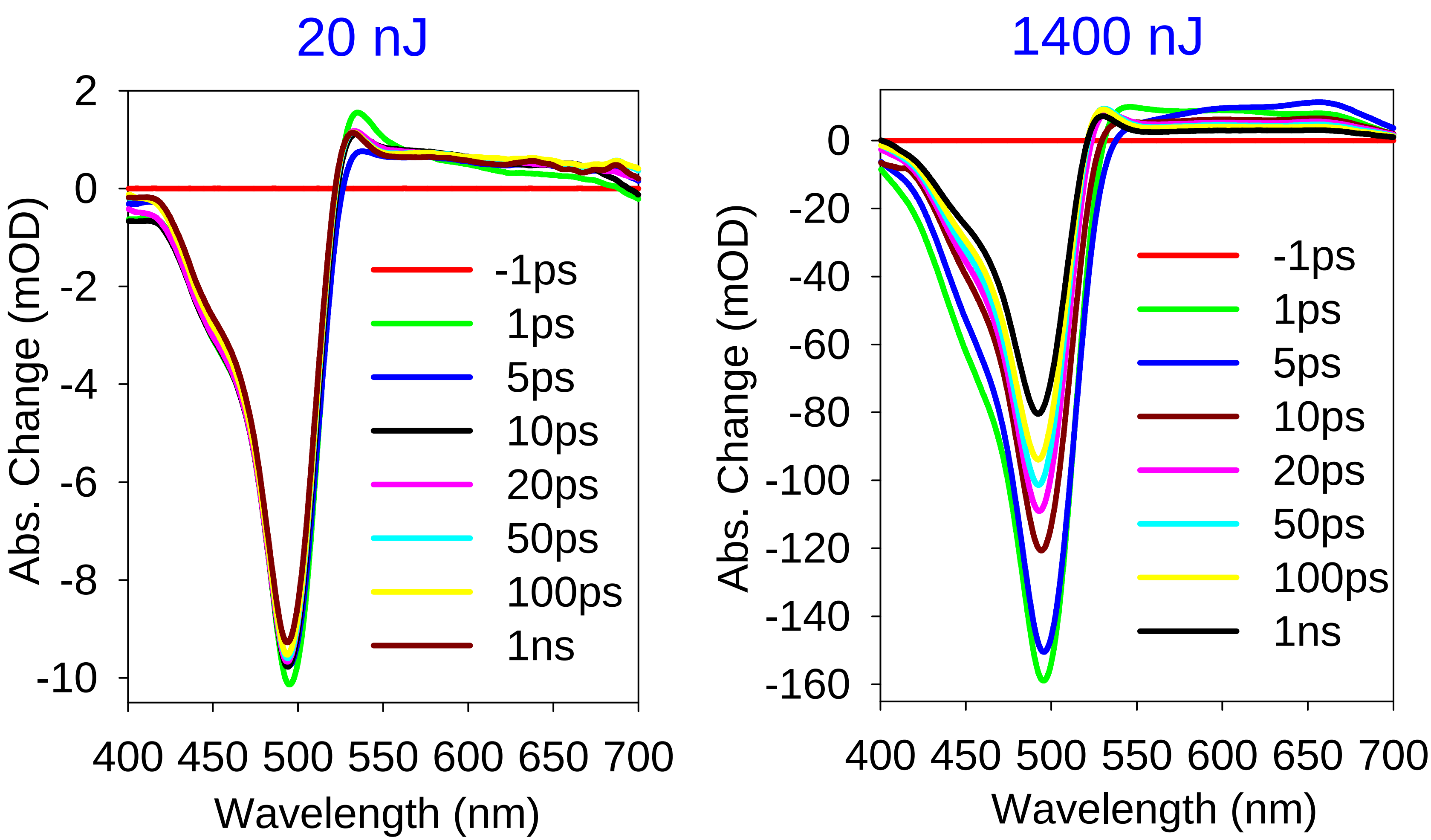


- Negligible energy transfer (no stimulated emission)
- Attributed to electron transfer
  - CdSe bleach recovery



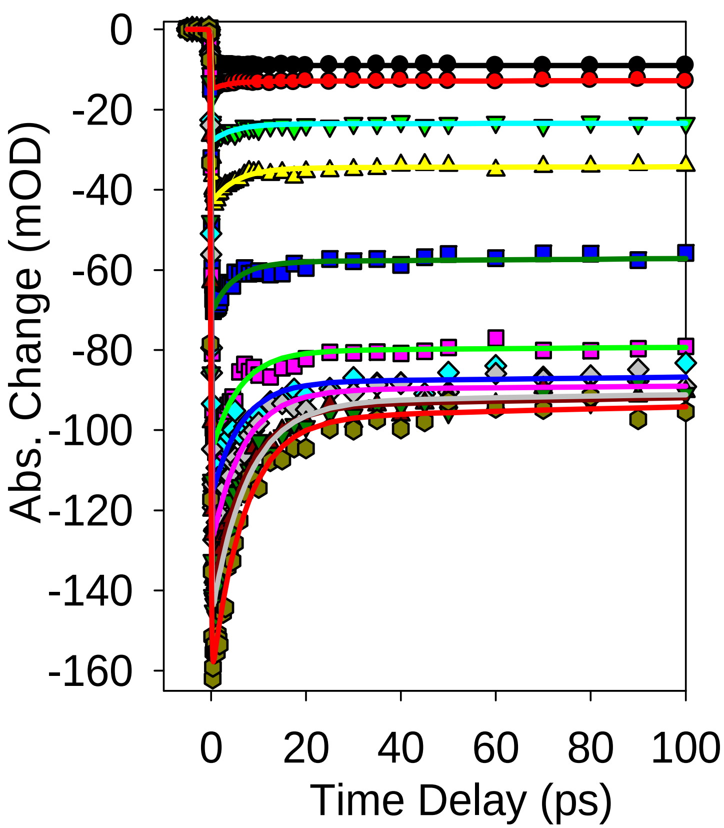
Norris, et al. PRB (1996) 53, 16338 Klimov, Science 2000, 287, 1011

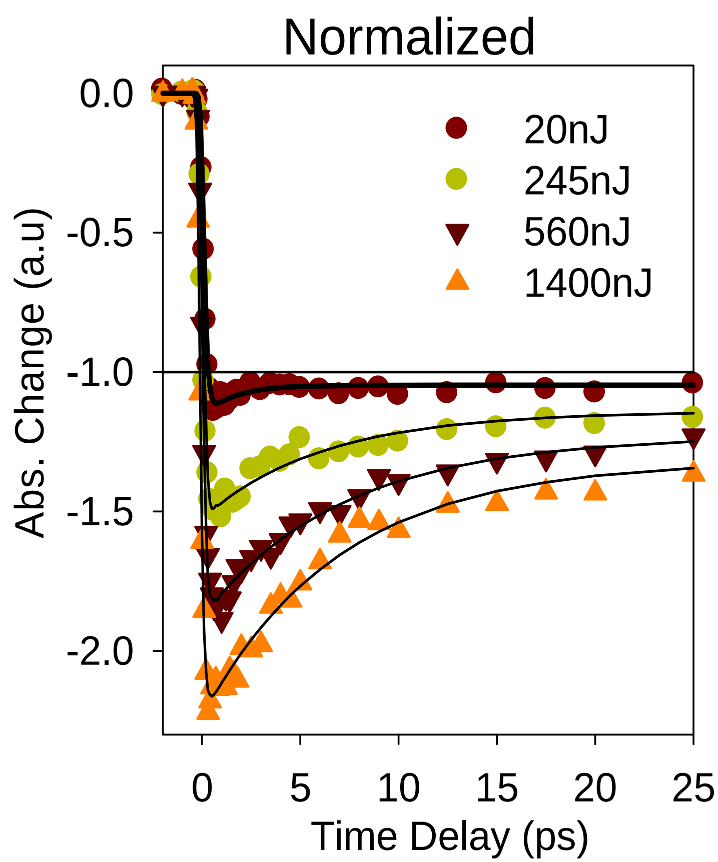
Multi-exciton generation in CdSe (by absorbing multiple photons)

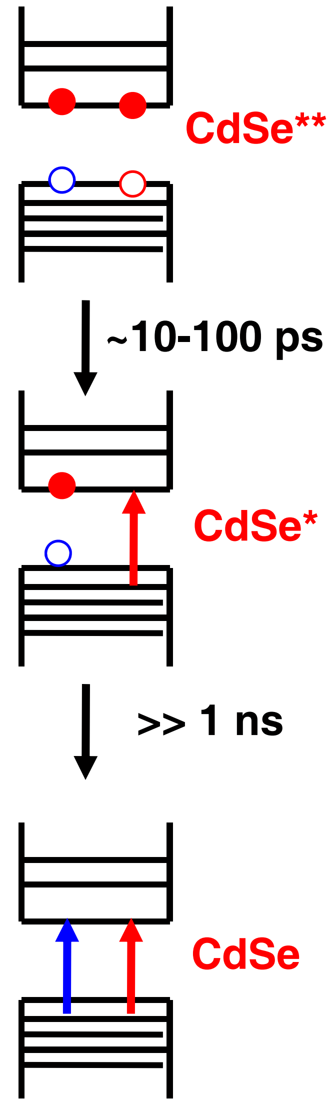


Klimov, Science 2000, 287, 1011

Multi-exciton generation in CdSe (by absorbing multiple photons)



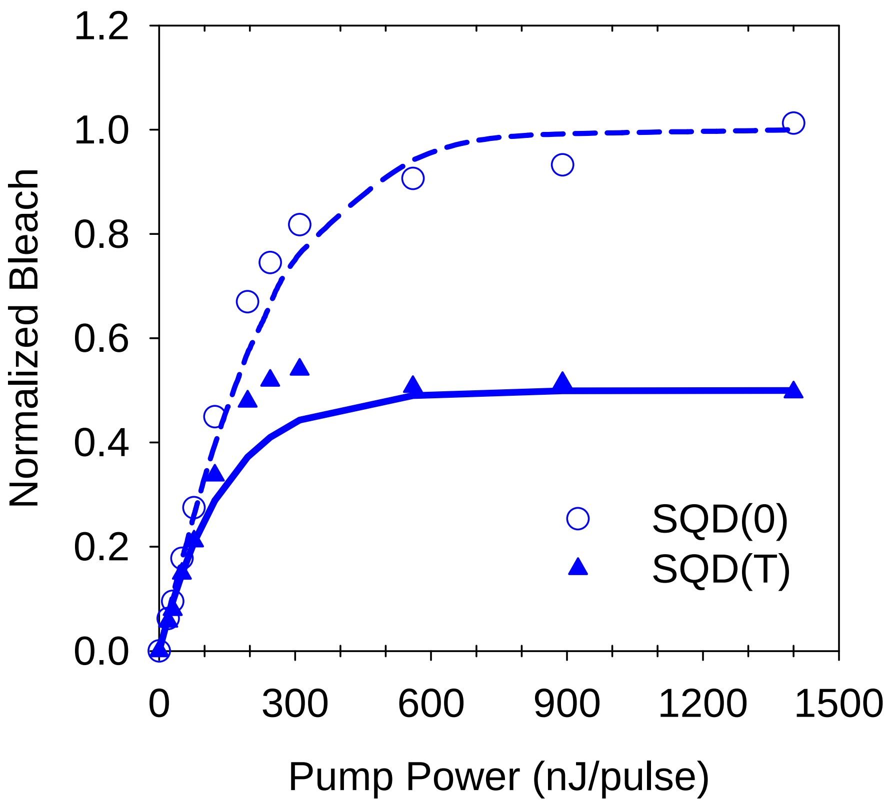




Fast decay –> exciton annihilation

Klimov, Science 2000, 287, 1011

Quantifying Multi-exciton generation in CdSe (by absorbing multiple photons)



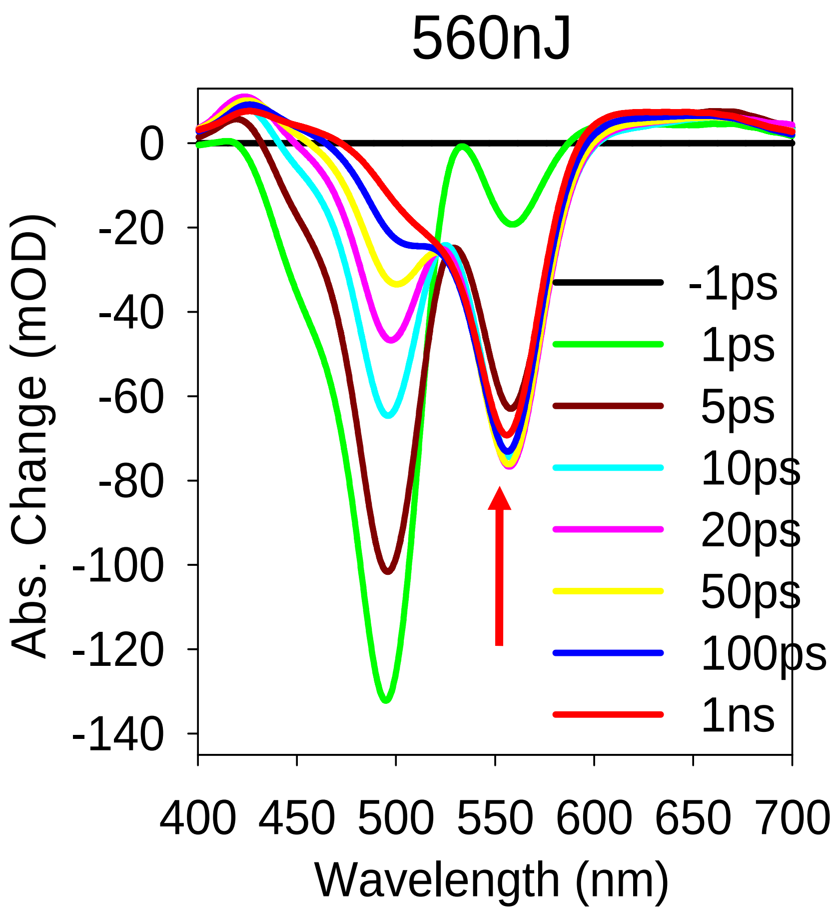
$$P_n = f(n,w) = \sum_n \frac{w^n}{n!} e^{-w}$$

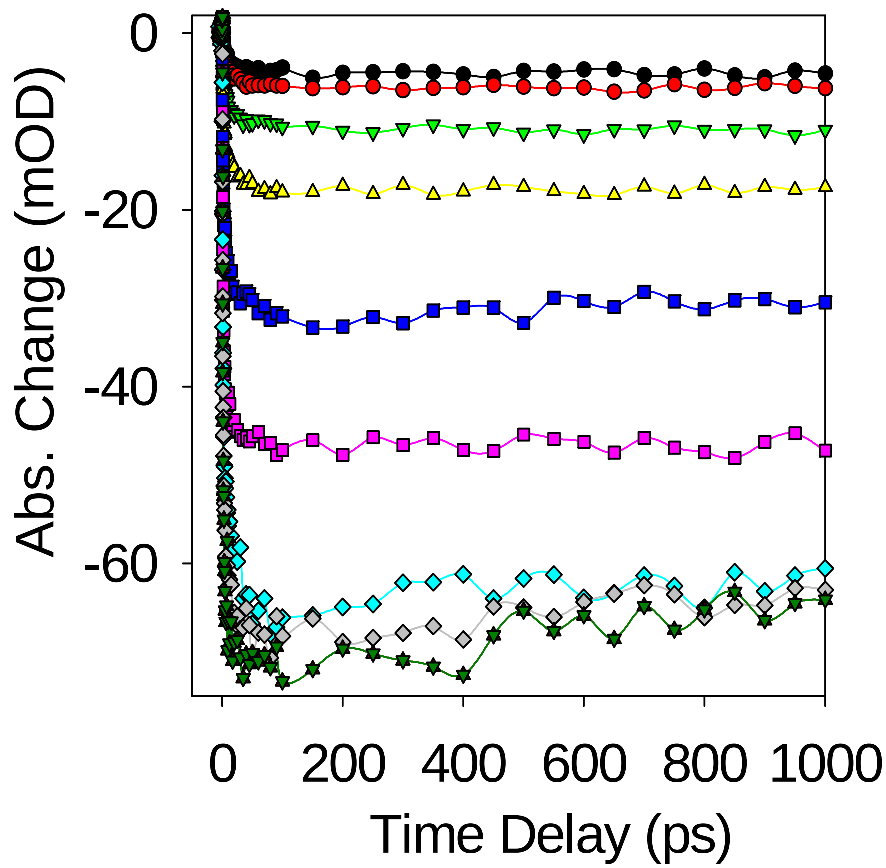
$$S_{QD}(0) = \frac{-\Delta S_{1s}(0)}{S_{1s}} = 1 - (1 + \frac{w}{2})e^{-w}$$

$$S_{QD}(T) = \frac{-\Delta S_{1s}(T)}{S_{1s}} = \frac{1}{2}(1 - e^{-w})$$

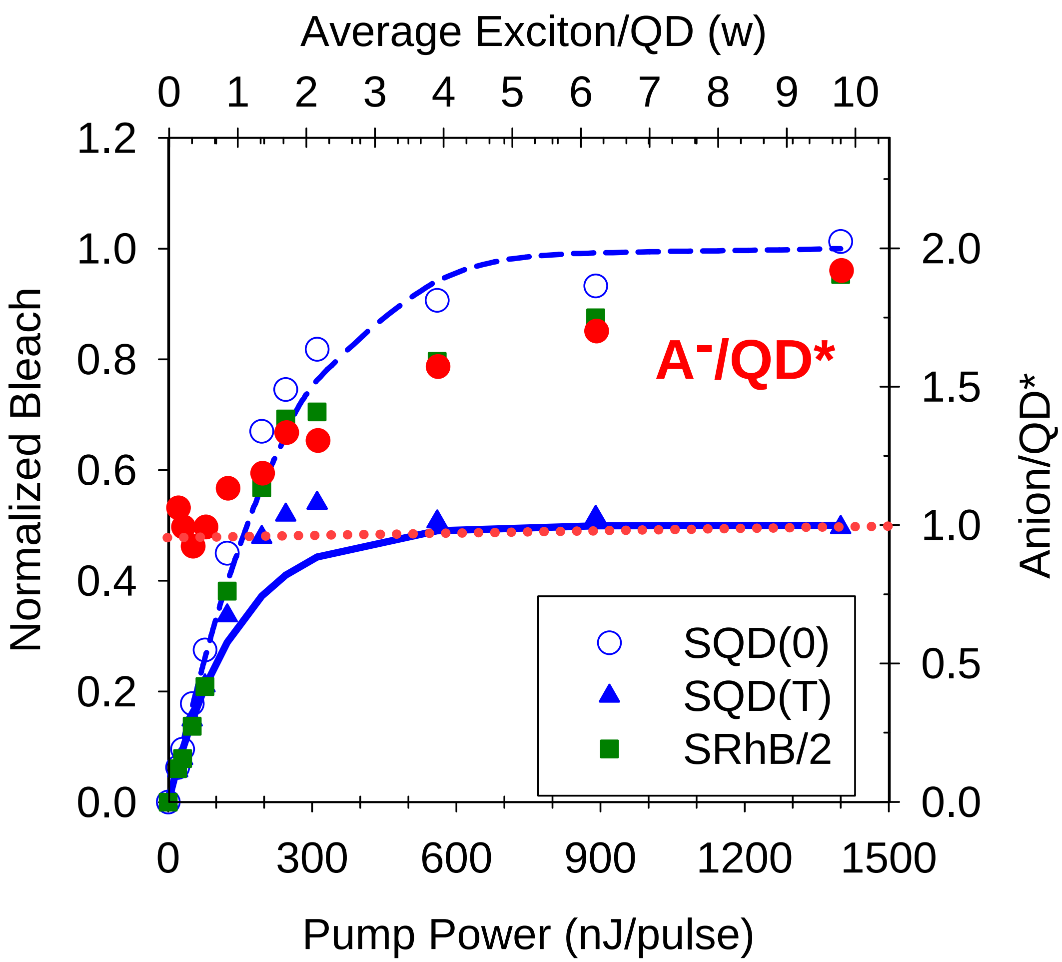
Klimov, Science 2000, 287, 1011

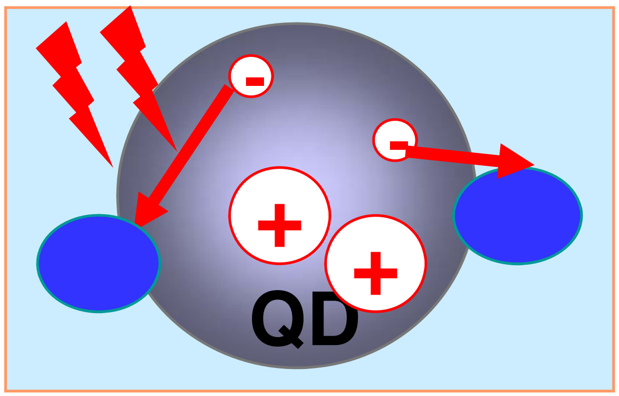
Multi-exciton Dissociation in CdSe/RhB





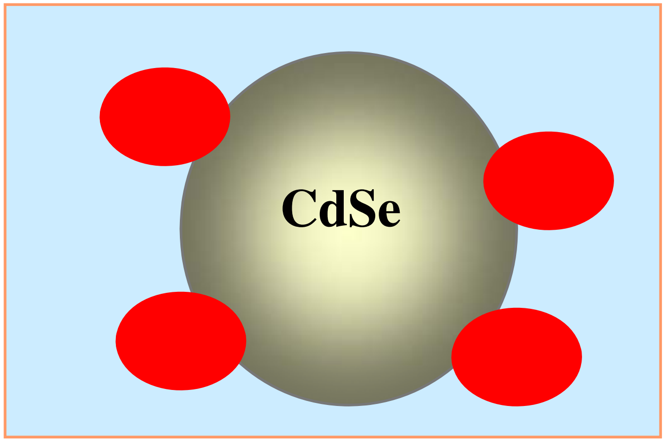
Multi-exciton Dissociation in CdSe/RhB





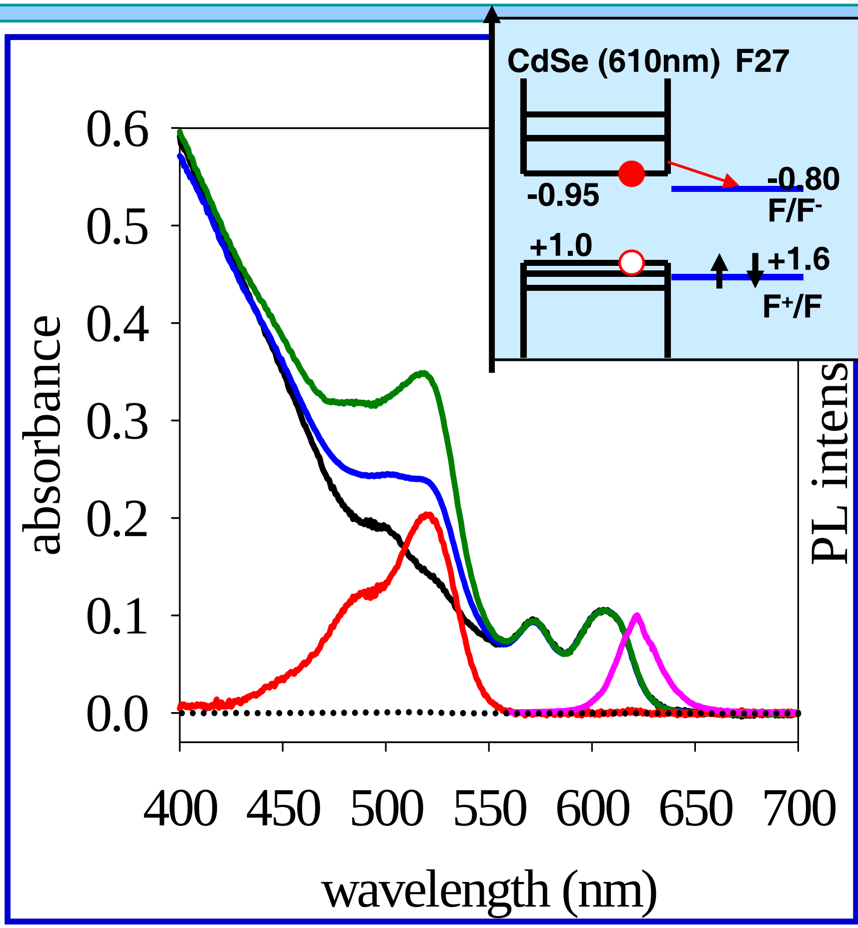
Dissociation of multiple excitons per QD (generated by absorbing multiple photons)

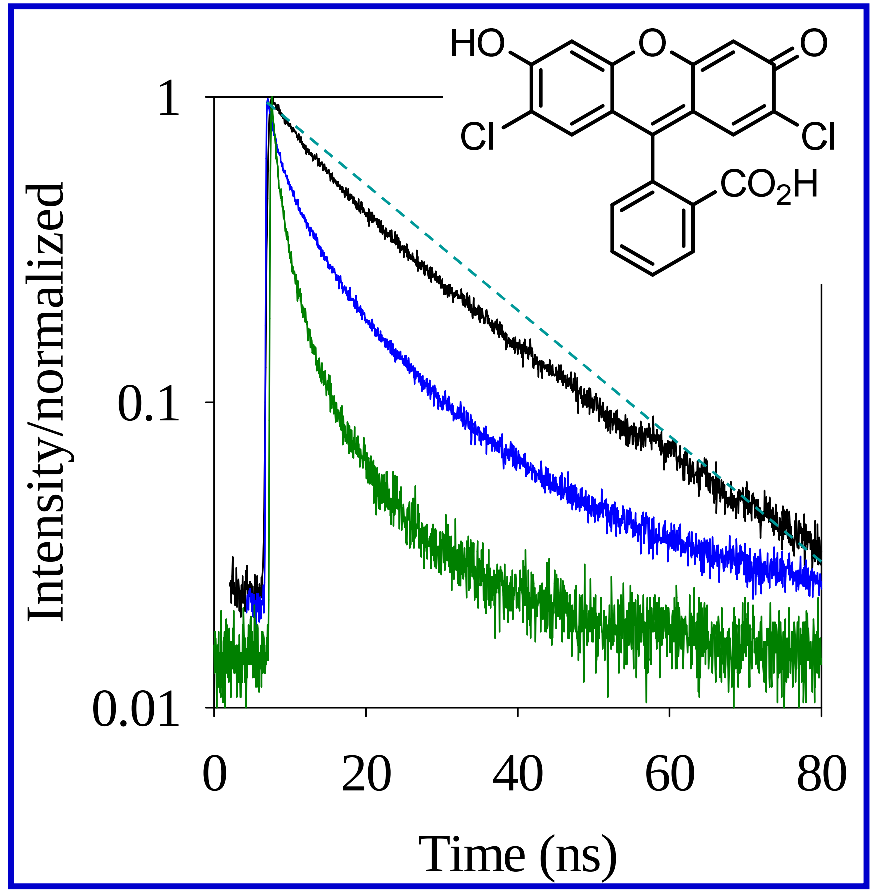
Outline



- Introduction-Multiexciton Generation
- Exciton dissociation pathway in CdS/RhB
- Size dependence in CdS/RhB
- Multiexciton dissociation in CdSe/RhB
- **Single particle electron transfer**

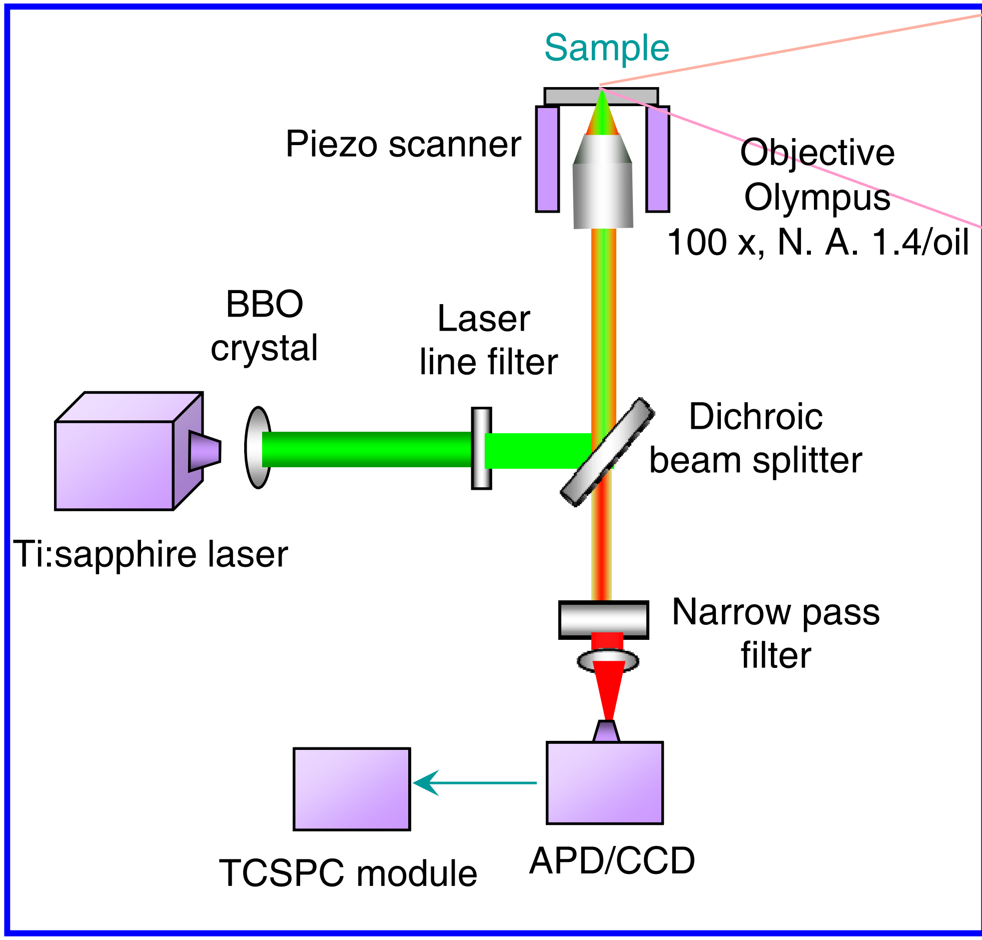
CdSe-Fluorescein: spectrum and energetics



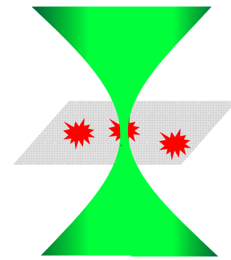


Origin of heterogeneity? (static and dynamic)

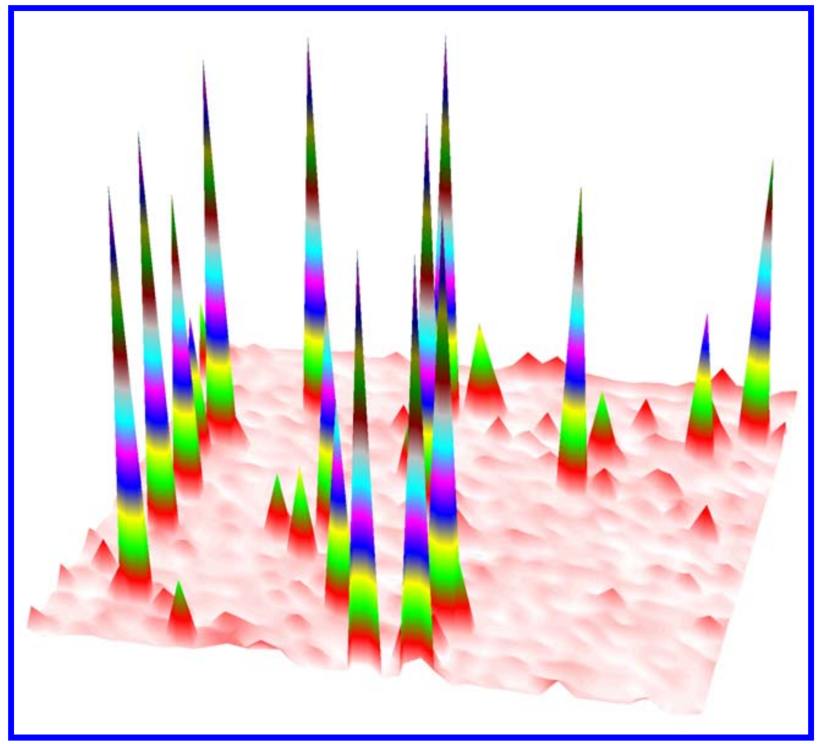
Single molecule/particle spectroscopy



Confocal Microscope Setup Attached with TCSPC Module

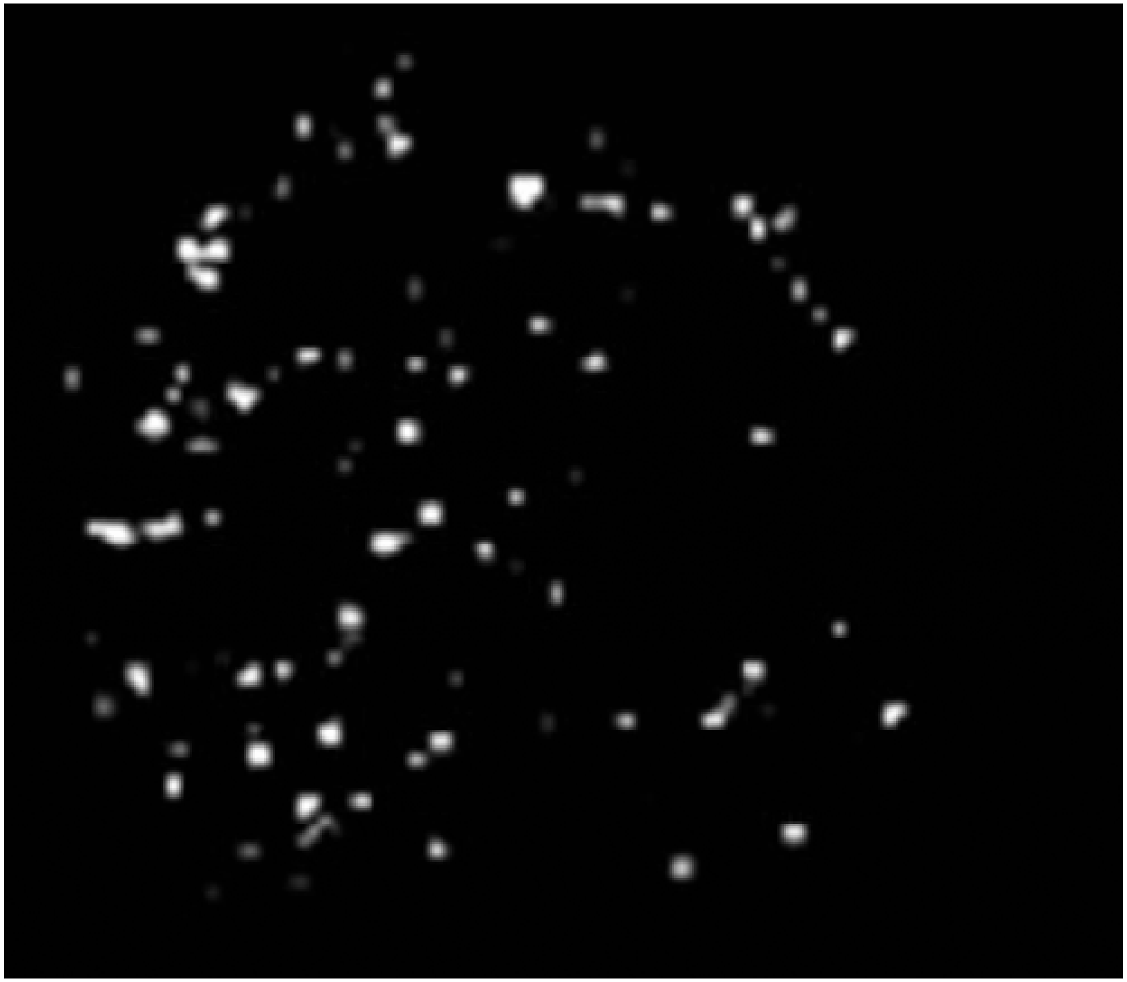


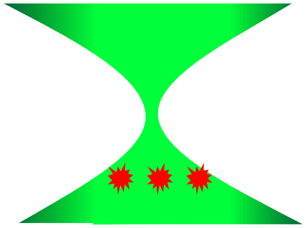
Confocal imaging



Single QDs on glass cover slip
40 µm x 40 µm

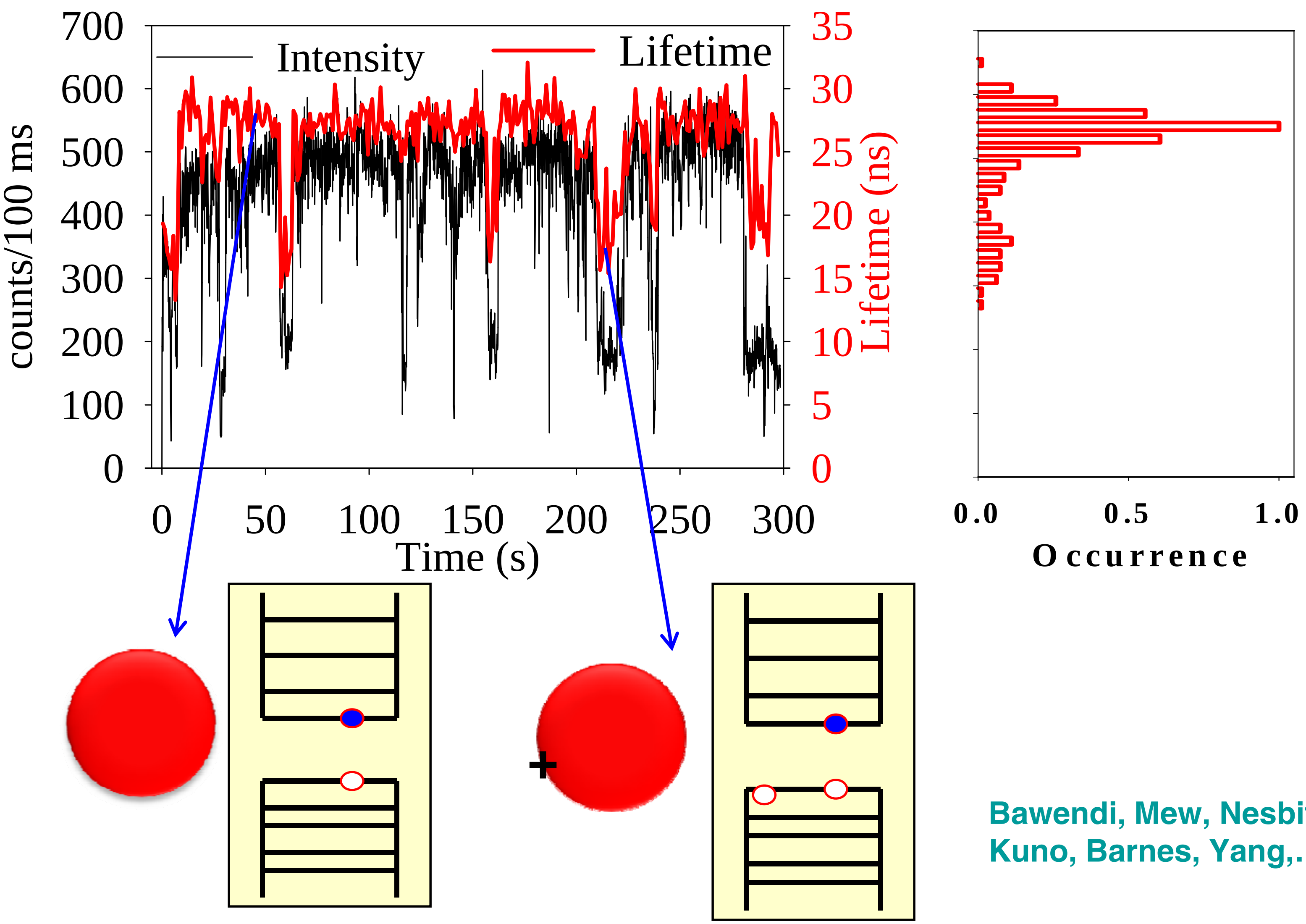
Single molecule/particle Imaging





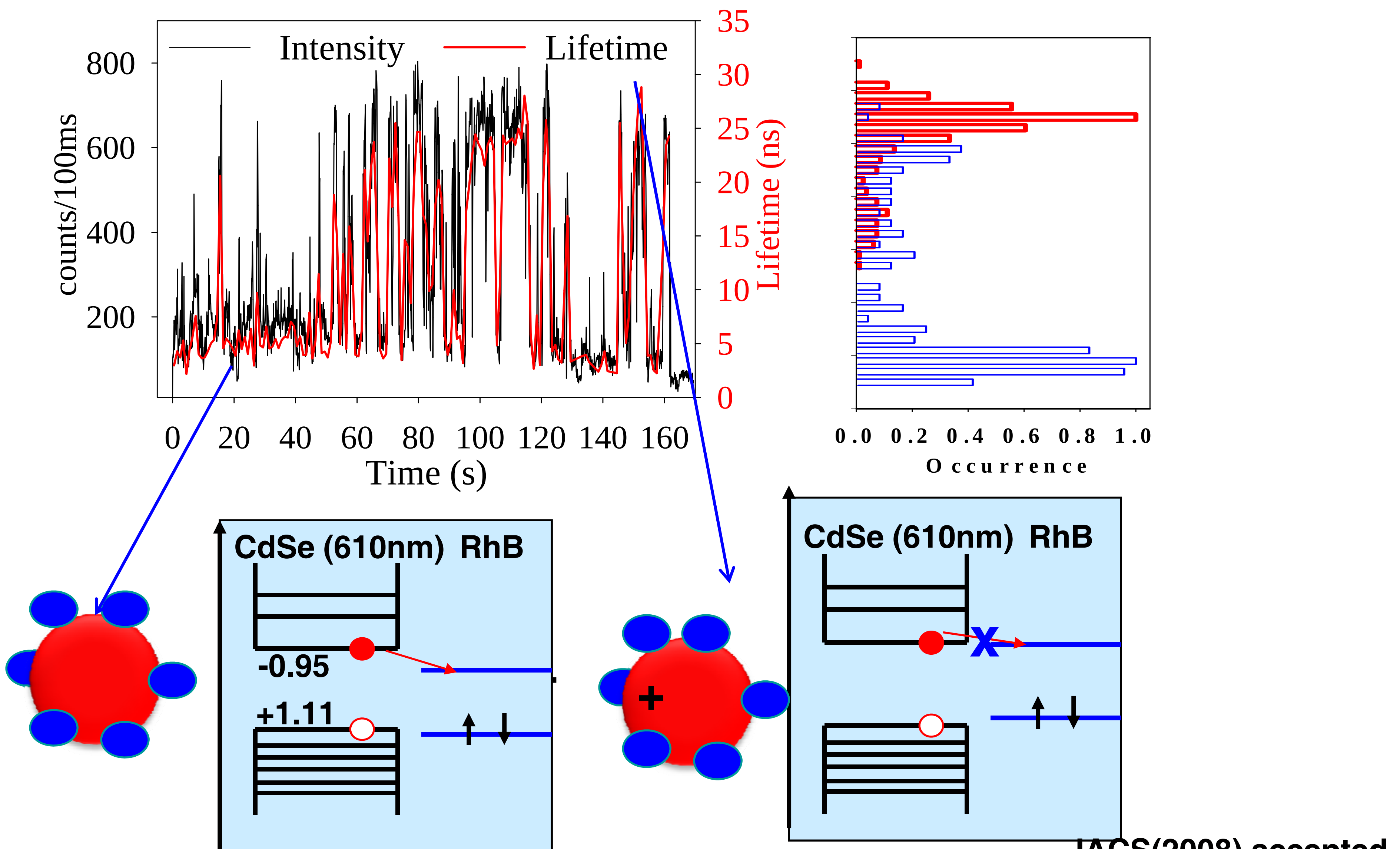
Wide field imaging

Fluctuation of intensity and lifetime in QDs



Bawendi, Mew, Nesbitt, Marcus, Kuno, Barnes, Yang,…..

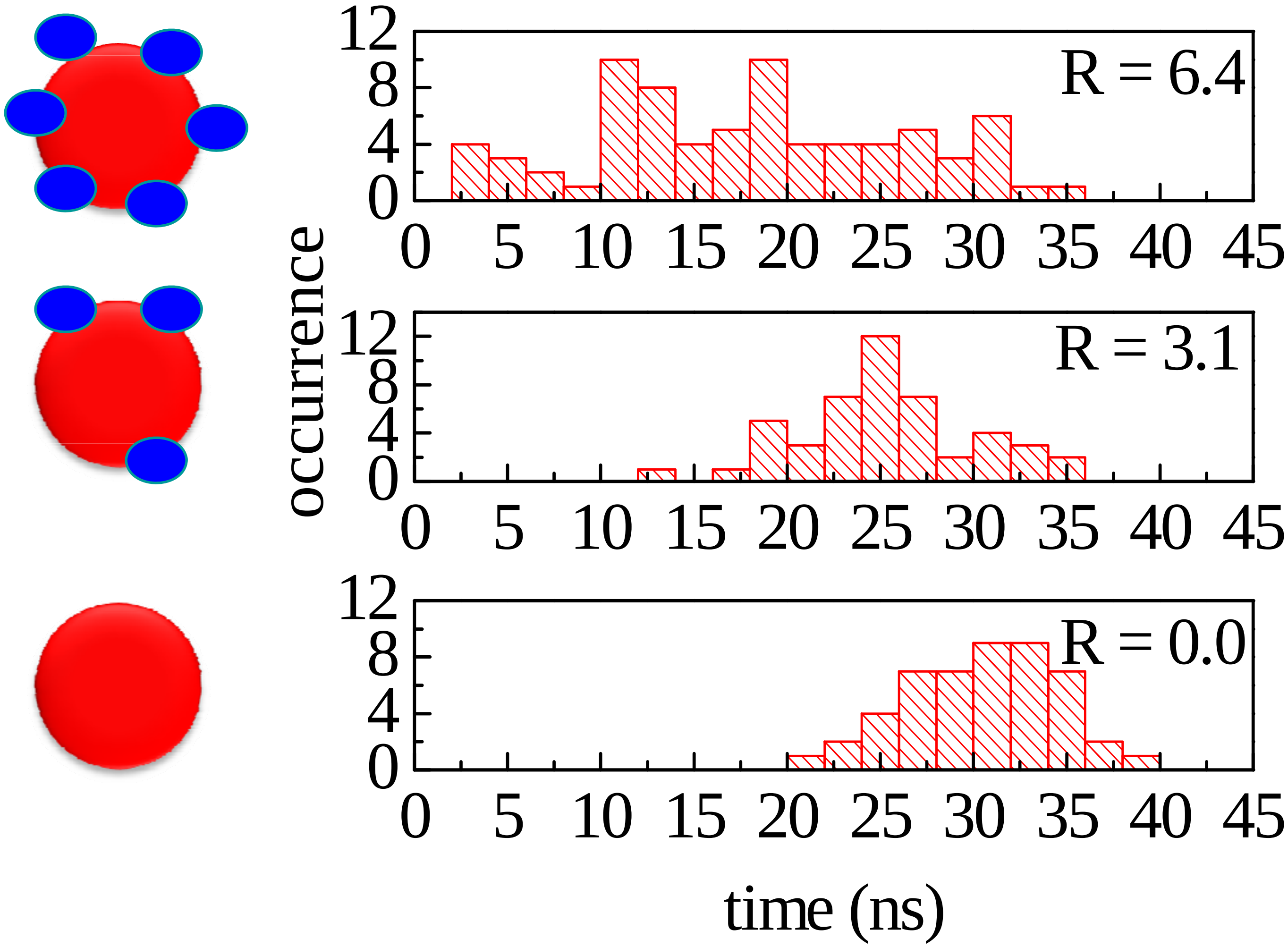
Fluctuation of ET activity in QD-adsorbates



JACS(2008) accepted

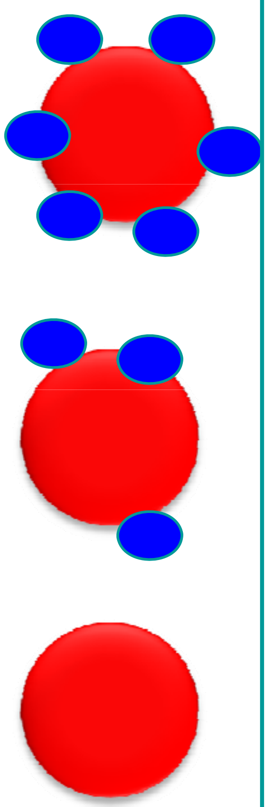
Deviation of ET activity in different QDs

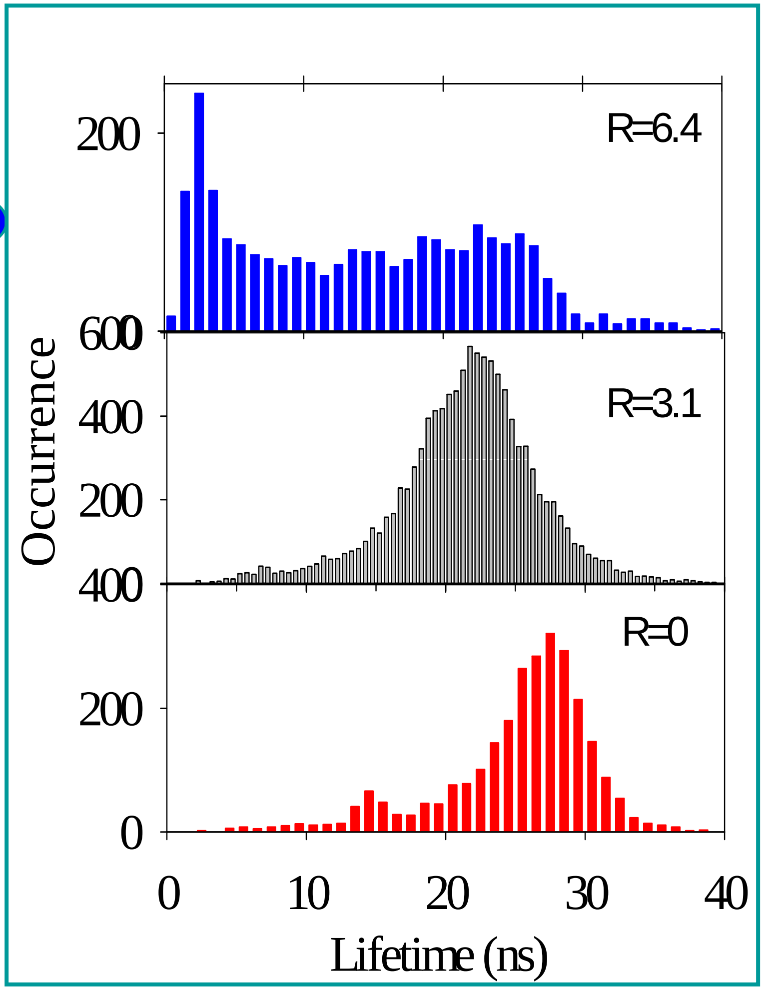
Distribution of average lifetime



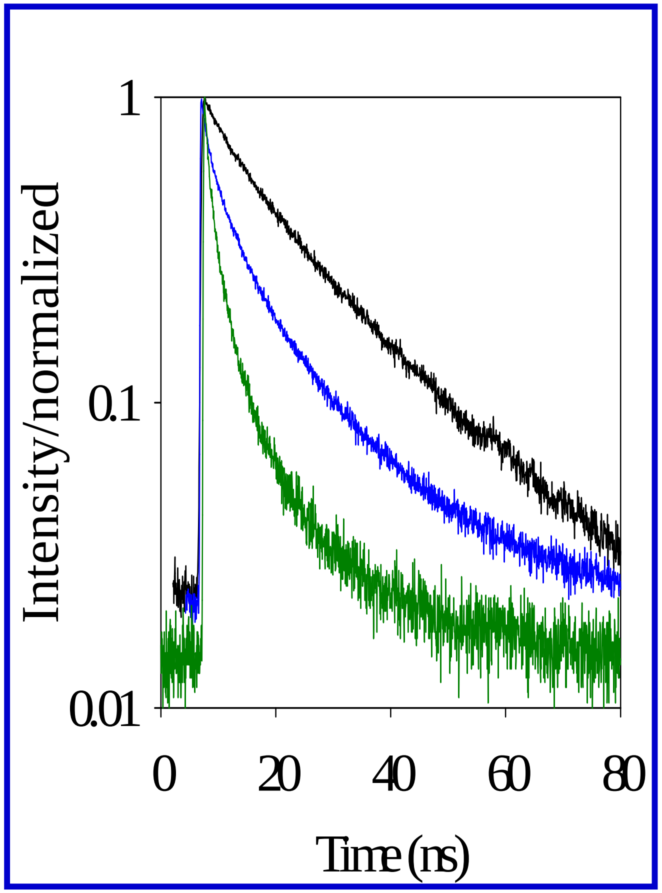
Unveiling the distribution of ensemble

Distribution of lifetime





Origin of non-exponential decay



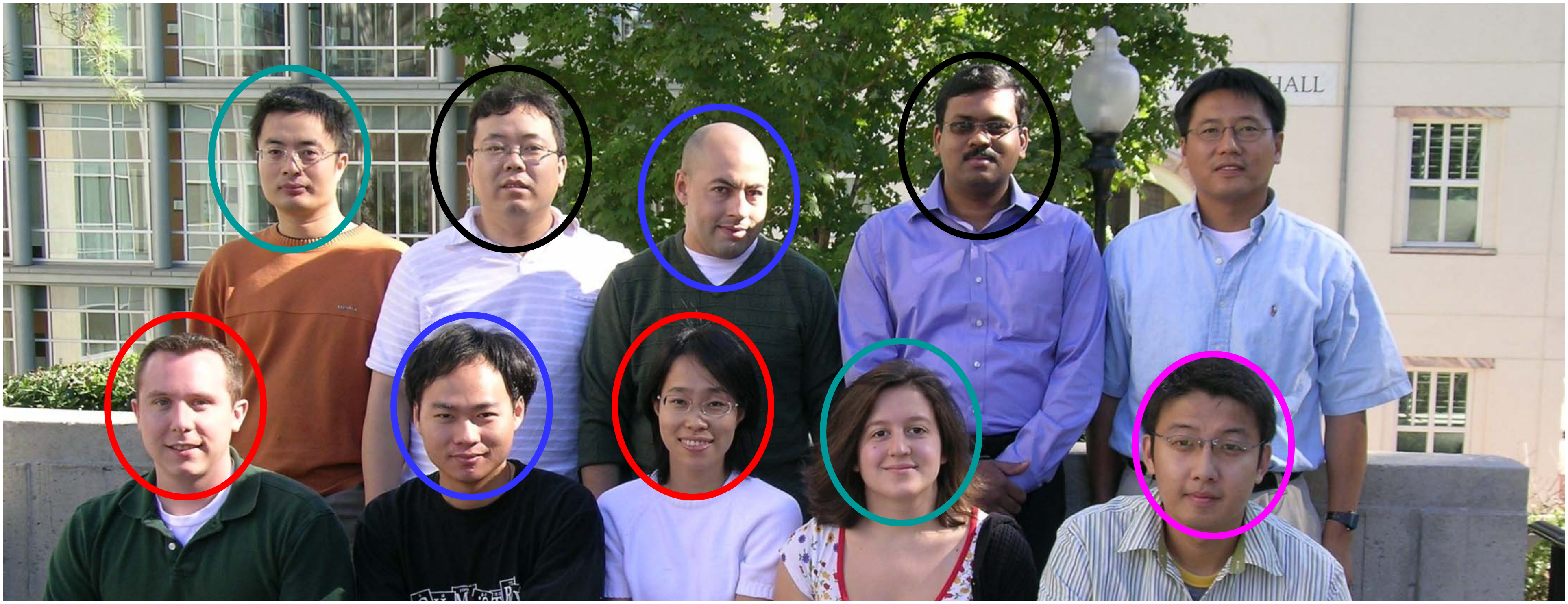
Summary

- Excitons in CdS QDs dissociates by ET to RhB
- ET rate decreases at larger particle size
- ET rate increases with the number of adsorbates
- Separation of multiple excitons (generated by multiple photons) in CdSe/RhB
- Large static and dynamic distribution of ET rate/activity in single QDs

Future directions

- Multiple exciton dissociation (generated by one photon) with better acceptors and in other QDs (PbSe)
- Use multi-exciton dissociation to probe MEG efficiency
- Characterize static and dynamic distribution by single QD spectroscopy

Acknowledgement



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